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# THE GEOCHEMISTRY OF HUNGARIAN BAUXITES PART I.

By

GY. BÁRDOSY

HUNGARIAN GEOLOGICAL INSTITUTE, BUDAPEST

As the first step in geochemical analysis of Hungarian bauxite, the author investigated the quantity and distribution of main bauxite elements (Al, Si, Fe, Ti, O, H). Investigations were based on nearly 28 000 analyses for each of these elements and evaluated with the aid of mathematical statistics.

The average chemical composition was determined for each of the known bauxite occurrences in Hungary. Moreover, the most important statistical parameters (median, mode, variance, etc.) and the frequency distribution were separately determined for each component within each occurrence.

These data have served as a basis for demonstrating some interesting geochemical relationships. Comparison of the frequency distribution of elements among individual localities yielded a new relation as to the quality of bauxite in function of its geographical location. At last, the quantity relations of the main elements for theoretical considerations concerning the distribution of alitic minerals as well as an attempt for the possible causes of this distribution can be explained.

## Introduction

The purpose of this study is the geochemical description of Hungarian bauxite. Its entire chemical composition will be treated, from the main elements to the trace components. The mineral bonds in which these elements tend to occur will be dealt with in the next step. Finally, conclusions will be drawn as to the possible genetics of Hungarian bauxites on the mineralogical and geochemical information obtained.

In compliance with the above set purposes, our work can be divided into four parts :

- I. Main elements of Hungarian bauxite (Al, Si, Fe, Ti, O, H).
- II. Accessory and trace elements in Hungarian bauxite.
- III. Mineralogical aspects of the chemical composition.
- IV. General geochemical evaluation, genetic considerations.

The present paper only contains Part I. The others will be published at a later date.

Hungarian bauxite occurs in geologically well-defined deposits which towards bedrock and cover are sharply bordered by readily detectable hiatuses and unconformities. However, the deposits contain argillaceous bauxite, bauxitic clay and even bauxite-free clay, besides the typical bauxite. Through-

out our investigations we will deal with the entire bauxite body. This is a geological as well as geochemical entity of which typical bauxite is only a part.

Up till now the bauxite-clay (allite-siallite) limit was universally defined by the so-called silica ratio (module), i. e. the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  weight percentage. The rocks with a ratio value below unity were considered as siallites; those above unity, as allites. However, this limit is purely arbitrary, lacking any kind of mineralogical or geochemical basis. Thus e. g. in kaolinite, almost only clay mineral of Hungarian bauxite, the silica ratio equals 0.85. Therefore, as much as 14.8 per cent of bauxite minerals may be present in a rock without raising the ratio above unity.

This circumstance led us to propose a different kind of classification, far more useful in delimiting gradually changing rock types of the bauxite body in a precise and geochemically correct manner.

1. Bauxite is defined as that part of the bauxite body in which more than 75 per cent of the whole aluminum content (equivalent to an  $\text{Al}_2\text{O}_3$  content of 55 to 45 per cent) is present in the form of (oxy)hydroxides.

2. Rocks containing 75 to 25 per cent of its aluminum in the form of (oxy)hydroxides are argillaceous bauxites ( $\text{Al}_2\text{O}_3$  content ranging from 45 to 35 per cent).

3. In bauxitic clay, less than 25 per cent of the total aluminum is present in the form of (oxy)hydroxides (35 to 30 per cent  $\text{Al}_2\text{O}_3$  content).

4. Clay is defined as containing no aluminum (oxy)hydroxides at all, entirely consisting of clay minerals ( $\text{Al}_2\text{O}_3$  content below 30 per cent).

The geochemical reasons for this sort of classification will be explained in the following publication.

On the basis of the above given definitions we have evaluated the data of 54 bauxite occurrences, the most important ones of the country. Their geographical and geological position is shown in Fig. 1. As to their geological structure we refer to a rich pertinent literature [8, 9, 10, 11]. For the sake of comparison, however, we have presented the stratigraphic columns of the more important occurrences (Fig. 2).

## Part I. Main elements of Hungarian bauxite (Al, Si, Fe, Ti, O, H)

The distribution of the six main elements in Hungarian bauxite is known by tens of thousands of analyses. Before treating the systematic geochemical use of this enormous material, it is necessary to consider the methods of analysing these elements, the accuracy of the methods, etc.

The main elements are assayed in most of the cases by routine analyses, whereby the rest of the constituents are left out of consideration. The analyses here referred to were made by the laboratories of the Chemical Works, Kelen-



föld, of the Gánt and Iszkaszentgyörgy Bauxite Mines and of the Ajka Alumina Factory. In all of these laboratories the analyses were carried out on identical principles, resulting in homogeneity of the material, necessary for statistical treatment.

The analyses were made according to the prescriptions of Industry, Norm MNOSZ 3295/52. The amount of aluminum, silicium, iron and titanium is given in the oxidic form, whereas the combined bauxite water is registered under "ignition loss". The latter and silica are determined by gravimetric means, ferric oxide by titration and titania by colorimetry. The amount of alumina is computed by subtracting the percentages of the above components from one hundred per cent.

In routine analyses the entire iron content is oxidated to the ferric stage and determined as ferric oxide. Ignition loss comprises, beside combined water, total bivalent sulphur in the form of sulphur dioxide, most of hexavalent sulphur (about 90 per cent) and total carbon dioxide. On the other hand, the amount of ignition loss is decreased by the oxidation of ferrous to ferric iron. The given values of titania and ferric oxide give the true amount of these components. The percentage of silica is somewhat increased by a part of the aluminum content entering in calcium and magnesium aluminate. The amount of this error increases with the silicium content. This deviation is corrected on the ground of several decades of laboratory experiences, by subtracting 1% from the silica percentage, if the same exceeds 10 weight per cent and 10 relative per cent of the silica content if the same is below 10 weight per cent. Every other accessory component is comprised in the  $\text{Al}_2\text{O}_3$  percentage, on the average, raising the value of the latter by 1 to 1,5 per cent.

The accuracy of routine analyses in absolute weight percentages is as follows :

$\text{SiO}_2$ below 10 per cent	$\pm 0,3$ per cent
above 10 " "	$\pm 0,5$ " "
$\text{Fe}_2\text{O}_3$	$\pm 0,3-0,5$ per cent
$\text{TiO}_2$	$\pm 0,1$ " "
ignition loss	$\pm 0,3-0,4$ " "

It is impossible to give the accuracy of  $\text{Al}_2\text{O}_3$  data, as it depends on the accuracy of determination, as well as on the percentual distribution of the components out of which amount they are indirectly computed.

### 1. Investigation of the distribution of main elements

The analysis population was grouped according to localities. With hardly any exceptions the analyses were made on samples from exploratory bores and/or shafts. The bauxite bodies were traversed by a more or less

regular network of bores and shafts. Furthermore, samples for analytical purposes were also taken at regular depth intervals (0,5 or 1,0 metres) at the shafts and drillings.

Thus the samples analyzed were evenly derived from the entire bauxite body. Consequently, the results of analysis reflect the actual chemical structure of the deposit.

A total of 27 875 routine analyses was used to characterize the 54 localities here treated. (The number of analyses belonging to the particular localities is listed in Table 11.) Geochemical evaluation for each element was separately carried out, by methods of mathematical statistics. The basic principles of the statistical methods used will be outlined at the appropriate point, but for more detailed information we must refer to pertinent literature [3, 56].

Only 29 of the 54 localities were treated in detail, namely those at which there was a sufficient number of analyses. In the case of the others the average composition was determined by computing only arithmetic means.

#### *Alumina content of bauxite*

To investigate this point, the frequency distribution of  $\text{Al}_2\text{O}_3$  percentages for each of the 29 localities was determined.\*

Considering the order of magnitude of alumina content, the grade width was set at one per cent. Because of our limited space we have to refrain from publishing these tables.

The average alumina content of Hungarian bauxite was generally considered to be 50 to 60 per cent. However, inspection of the frequency histograms shows that it varies between much broader limits. For further insight, extremal values were listed in Table 1. According to this Table, the greatest alumina content hitherto observed in Hungarian bauxite is 76,8 per cent, at the Nagy-harsány locality. The maximum alumina content is 60 to 73 per cent in the rest of the greater occurrences; 50 to 60 per cent in the smaller ones.

Minimum content usually varies between 20 to 30 per cent. Values smaller than these were restricted to the Nézsa (15,0), Harasztos (16,0) and Cseres (19,0) localities.

As these extremes may eventually be isolated ones, one per cent of the total number of analyses was left off from both extremities of the distribution table and extremal percentages were subsequently redetermined. The maximum thus obtained was generally between 55 and 65 per cent. Greater values, consequently, do not occur except in negligibly small parts — less than one per cent — of the bauxite body. The only exception is the Nagy-harsány field where even this reduced extreme amounted to 74 per cent. The minimum values

\* The frequency distribution table gives the number of analyses in each of the statistical classes, in percents of the total number of analyses (see 3.5.6).



**Table 1**  
*Geochemical parameters of  $Al_2O_3$  content*

Occurrence	Extremals				Central values			Scatter	
	lower		upper		Arith- metic mean	Median	Mode	Vari- ance	Standard devia- tion
	100%	99%	99%	100%					
Sümeg .....	30,0	30,5	62,0	66,0	47,4	49,4	54,5		
Nyirád: Darvastó.....	22,0	29,5	60,5	73,0	48,2	50,1	52,5	51,7	$\pm 7,2$
„ Deákihegy .....	25,0	32,0	62,0	71,0	52,2	55,2	57,5	60,8	$\pm 7,8$
„ Táncsics II. ....	23,0	31,5	65,5	75,0	47,6	48,3	56,5	73,3	$\pm 8,6$
„ Izamajor .....	26,0	32,0	63,5	72,0	51,1	54,4	56,5	61,5	$\pm 7,8$
Zalahaláp .....	27,0	29,0	47,5	55,0	36,9	36,6	36,5		
Szőc: Vargatanya .....	28,0	30,0	55,0	57,0	41,1	40,2	39,5		
„ Félix II. ....	25,0	30,5	57,0	62,0	43,6	43,3	40,5	31,2	$\pm 5,6$
„ Dorottya—Szárhegy	25,0	29,5	54,5	60,0	43,8	44,3	48,5	27,6	$\pm 5,3$
„ Nyíreskút .....	27,0	30,0	57,5	68,0	44,4	45,7	49,5		
„ Malomvölgy .....	23,0	28,5	55,5	66,0	41,8	41,3	41,5	32,1	$\pm 5,7$
Nagyvázsony .....	24,0	29,0	46,5	56,0	36,3	36,0	35,5		
Halimba: Cseres.....	19,0	34,0	63,5	71,0	48,5	47,6	46,5	51,9	$\pm 7,2$
„ Tormáskút .....	23,0	33,5	62,5	67,0	50,0	50,6	53,5	39,7	$\pm 6,3$
Városlőd: Öreghegy .....	25,0	32,0	63,5	68,0	46,9	47,1	54,5 (38,5)	66,4	$\pm 8,1$
Fenyőfő .....	28,0	30,5	50,5	51,0	40,8	40,7	39,5		
Dudar .....	25,0	25,5	49,0	52,0	40,0	39,8	39,5		
Eplény .....	34,0	34,5	57,0	60,0	46,9	47,6	47,5		
Alsópere .....	27,0	32,5	61,5	63,0	47,2	47,2	48,5	44,4	$\pm 6,7$
Tés.....	25,0	28,5	51,5	52,0	40,6	40,7	40,5		
Iszkaszentgyörgy:									
Kincses-József .....	24,0	34,5	59,5	65,0	50,9	52,0	52,5	22,6	$\pm 4,8$
„ Rákhegy .....	29,0	35,5	61,5	70,0	52,7	53,8	54,5	26,1	$\pm 5,1$
Gánt: Bagolyhegy .....	25,0	37,0	63,5	71,0	50,0	50,3	50,5	28,3	$\pm 5,3$
„ Harasztos, Meleges, Újfeltárás .....	16,0	29,5	68,0	73,0	46,8	46,3	44,5	45,8	$\pm 6,8$
Óbarok—Újbarok— Vázsony psz. ....	28,0	30,5	60,5	68,0	45,7	46,4	46,5	54,3	$\pm 7,4$
Nagyegyháza .....	22,0	28,0	57,5	63,0	44,0	44,2	38,5	47,7	$\pm 6,9$
Pilisszántó .....	21,0	22,5	60,0	62,0	42,1	41,3	41,5		
Nézsza .....	15,0	24,0	63,5	65,0	44,9	43,6	58,5		
Nagyharsány .....	27,0	30,0	74,0	77,0	58,1	62,0	62,5		

also became much more homogeneous, falling to 25 and 35 per cent on the average. The importance of values smaller than these is negligible as related to the entire bauxite body.

The distribution of  $\text{Al}_2\text{O}_3$  percentages between the given extremities may, however, exhibit intense variations. To express the intensity of aluminium accumulation in a concise manner, central values such as the arithmetic mean, the median and the mode had to be computed. These values were determined for all of the 29 localities (Table 1).

As these values were derived from routine analyses, they contain 1 to 1,5 per cent of accessory and trace elements.

The greatest arithmetic mean, 56,7 per cent,\* was obtained from the Nagyharsány bauxite. In 20 of the 29 localities the arithmetic mean ranged from 40 to 50 per cent. However, we may state that the average composition of our bauxite bodies show marked differences—greater than should be expected in a homogeneous rock. The reason for this is that the bauxite body is a complex of different varieties of rock.

Last but not least we have computed from the arithmetic means of individual occurrences the  $\text{Al}_2\text{O}_3$  content of average Hungarian bauxite. In so doing the means of individual occurrences were weighed by the size of the occurrence. A result 44,8 per cent was in this way obtained.

It was considered necessary to determine the median beside the arithmetic mean because the former is more likely to express real chemical composition. The arithmetic mean is all too sensitive to values lying far from the average, small changes of which may cause it to alter significantly. However, being the percentage by which the number of analyses is divided in two equal parts, the median is insensitive to the skewness of the distribution. To facilitate evaluation the differences of medians and arithmetic means were listed in Table 2 in a decreasing order of the arithmetic mean. The table shows a remarkable relationship, namely that in deposits of greater  $\text{Al}_2\text{O}_3$  percentage the median is greater than the arithmetic mean, whilst the opposite is observed in deposits of smaller  $\text{Al}_2\text{O}_3$  content. On the other hand, the differences are larger in the former case (1 to 4 per cent) and smaller in the latter (generally below one per cent).

The cause of this phenomenon is, in our opinion, the one-directional trend of the bauxitization process which tends to make asymmetrize the originally symmetric aluminium distribution. Of course, this process will be most advanced in bauxite bodies of greater  $\text{Al}_2\text{O}_3$  content.

Mode, the third central value, yields the  $\text{Al}_2\text{O}_3$  percentage of maximum frequency, i. e. the location of the peak of the distribution curve. In comparing

\* The arithmetic mean is computed by the formula





























$$A = \frac{\sum_i^n w_i a_i}{\sum_i^n w_i}$$

where  $a_i$  is the middle percentual  $\text{Al}_2\text{O}_3$  content of the  $i^{\text{th}}$  class;  $w_i$  the number of analyses (frequency) in that class; and  $n$  the number of non-empty classes.



Table 2

*Comparison of average  $Al_2O_3$  content with other characteristic parameters*

Occurrence	Arithmetic mean	Difference		Age of immediate cover	Shape of histogram
		to median	to mode		
Nagyharsány	58,1	+ 3,9	+ 4,4	Aptian	
Rákhegy	52,7	+ 1,1	+ 1,8	l. Eocene	
Deákihegy	52,2	+ 3,0	+ 5,3	l. Eocene	
Izamajor	51,1	+ 3,3	+ 5,4	l. Eocene	
Kincses-József	50,9	+ 1,1	+ 1,6	l. Eocene	
Tormáskút	50,0	+ 0,6	+ 3,5	Turonian	
Bagolyhegy	50,0	+ 0,3	+ 0,5	l. Eocene	
Cseres	48,5	- 0,9	- 2,0	l. Eocene	
Darvastó	48,2	+ 1,9	+ 4,3	Pleistocene + l. Eocene	
Táncsics II	47,6	+ 0,7	+ 8,9	Tortonian	
Sümeg	47,4	+ 2,0	+ 7,1	m. Eocene	
Alsópere	47,2	± 0,0	+ 1,3	Aptian	
Városlőd	46,9	+ 0,2	+ 7,6	l. Eocene	
Eplény	46,9	+ 0,7	+ 0,6	Pleistocene + l. Eocene	
Óbarok-Ujbarok	45,7	+ 0,7	+ 0,8	u. Oligocene	
Nézsza	44,9	- 1,3	+ 3,6	m. Eocene	
Nyíreskút	44,4	+ 1,3	+ 5,1	l. Pliocene + l. Eocene	
Nagyegyháza	44,0	+ 0,2	- 5,5	u. Oligocene	
Doróttya-Szárhegy	43,8	+ 0,5	+ 4,7	l. Eocene	
Félix II	43,6	- 0,3	- 3,1	l. Eocene	
Pilisszántó	42,1	- 0,8	- 0,6	l. Eocene	
Malonvölgy	41,8	- 0,5	- 0,3	l. Eocene	
Vargatanya	41,1	- 0,9	- 1,6	l. Eocene	
Fenyőfő	40,8	- 0,1	- 1,3	l. Eocene	
Tés	40,6	+ 0,1	- 0,1	Aptian	
Dudar	40,0	- 0,2	- 0,5	l. Eocene	
Zalahaláp	36,9	- 0,3	- 0,4	Tortonian	
Nagyvázsony	36,3	- 0,3	- 0,8	Pliocene	

the mode with the former two central values we obtain the deviation of computed means from the most frequent value of the deposit. In the case of ideal rock composition the three values should approximately coincide.

The differences of modes and arithmetic means are also listed in Table 2. The results are similar to those obtained for medians, inasmuch as the mode is greater than the arithmetic mean in deposits of higher, and smaller in deposits of lower alumina content. Their differences in the former case are likewise greater, often reaching 5 to 9 per cent. Consequently, the distribution is most askew in cases of more intense alumina accumulation.

A further step in analyzing the frequency distribution was made by relegating the frequency percentages of the distribution tables into three groups, namely :

1.  $\text{Al}_2\text{O}_3$  content above 48 per cent;
2.  $\text{Al}_2\text{O}_3$  content 48 to 37 per cent;
3.  $\text{Al}_2\text{O}_3$  content below 37 per cent.

The limiting values were chosen on the basis of a two-variable correlation reckoning (to be later described in a following paper) which showed that if 75 per cent of total aluminum in the given rock occurred in a hydroxidic form the most probable value of its alumina content was 48 per cent. In case of 37 per cent of average alumina content, 25 relative per cent is hydroxide and 75 per cent is in the clay minerals.

As mentioned in the introduction, rocks containing three quarters or more of their total aluminum in (oxy)hydroxidic form are termed bauxites, those with 25 to 75 per cent, argillaceous bauxite, and those below, bauxitic clay. Thus by above classification it becomes possible to determine the percentage of bauxite, argillaceous bauxite and bauxitic clay indirectly from their alumina content in the individual occurrences.

This triple grouping was illustrated in a diagram (Fig. 3) showing the localities in decreasing order of magnitude of the first group. ( $\text{Al}_2\text{O}_3$  above 48 per cent.)

In Hungarian bauxite occurrences the proportions of these groups greatly vary. The deposit may contain a maximum of 87,4 per cent of bauxite (Rák-hegy). There are four more occurrences (Kincses-József, Izamajor, Deáki-hegy and Nagyharsány) where some three quarters of the deposit consist of pure bauxite. In most of the occurrences, however, the amount of pure bauxite ranges from 20 to 70 per cent.

On the other hand, there are a number of localities where no more than 1 to 5 per cent of the entire deposit consists of alumina-rich bauxite (Tés, Dudar, Fenyőfő, Zalahaláp, Nagyvázsony).

It is remarkable that the decrease of bauxite content is accompanied by the increase of the argillaceous bauxite group instead of that of bauxitic clay.



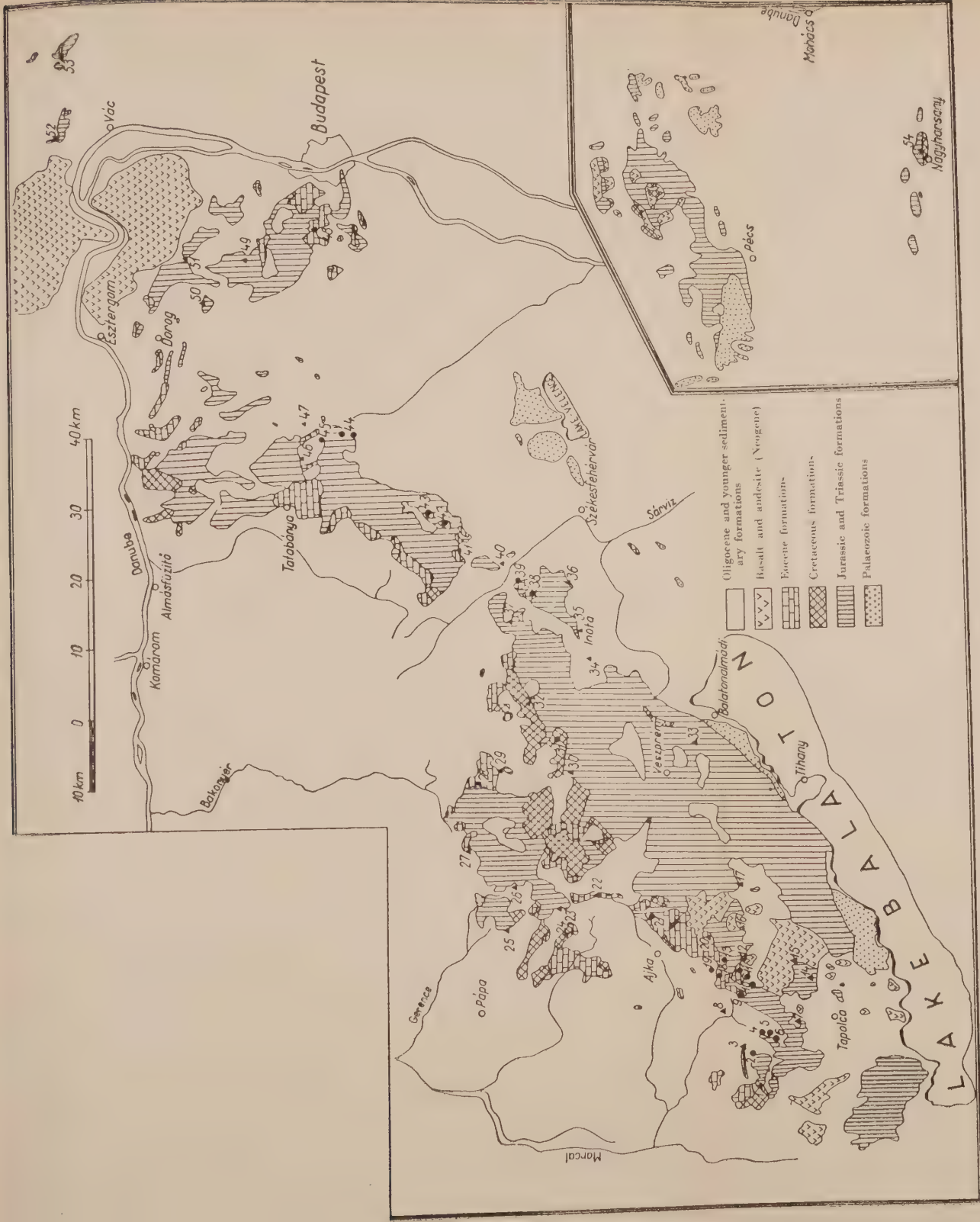


Fig. 1. Geological situation of Hungarian bauxite occurrences.

Serials of bauxite occurrences:

1. Sümeg
2. Nyírad : Darvasfő
3. Nyírad : Tüskés-major
4. Nyírad : Deák-hegy
5. Nyírad : Táncsics II.
6. Nyírad : Izumajor
7. Zalahaláp : Véndekhegy
8. Nyírad : basin N.
9. Szóc : Vargatanya
10. Szóc : Félix II.
11. Szóc : Dorottya—Szárhegy
12. Szóc : Nyíreskút
13. Szóc : Malomvölgy
14. Hegyesd
15. Monostorapáti
16. Ócs
17. Nagyvácsány
18. Halimba : Csere

19. Halimba : Tormáskút
20. Padrag : Kábhely S.
21. Városlőd : Öreghegy
22. Csetbánya
23. Iharkút
24. Bakonyjákó
25. Ugod
26. Bakonybél : Hubertlak
27. Fenyőfő
28. Csesznek : Kővölgy-árok
29. Dudar
30. Eplény
31. Alsópere
32. Tes
33. Szentkirályszabadja
34. Várpalota
35. Inota
36. Csór

37. Isztimér : Vöröshegy
38. Iszka-szentgyörgy : Kincses-József
39. Iszka-szentgyörgy : Rákhegy
40. Magyaralmás
41. Csákerény
42. Gánt : Bagolyhegy
43. Gánt : Harasztos, Újteltárás
44. Óbarok—Újbarok—Vázsony psz.
45. Nagycsáka
46. Mesterberek
47. Tükrősmajor
48. Budakeszi
49. Pilisvörösvár
50. Piliscsaba
51. Pilisszántó
52. Szendehely : Naszál
53. Nézsa
54. Nagyvácsány

● Larger occurrences thoroughly investigated  
▲ Less thoroughly known, smaller occurrences, and superficial indications











Thus most of the non-bauxitic parts of the deposit consists of argillaceous bauxite. The amount of bauxitic clay, i. e. of rock containing less than 37 per cent of alumina, varies from 5 to 20 per cent. The Zalahaláp and Nagyvázsöny

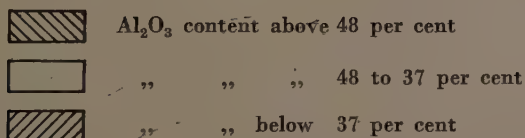
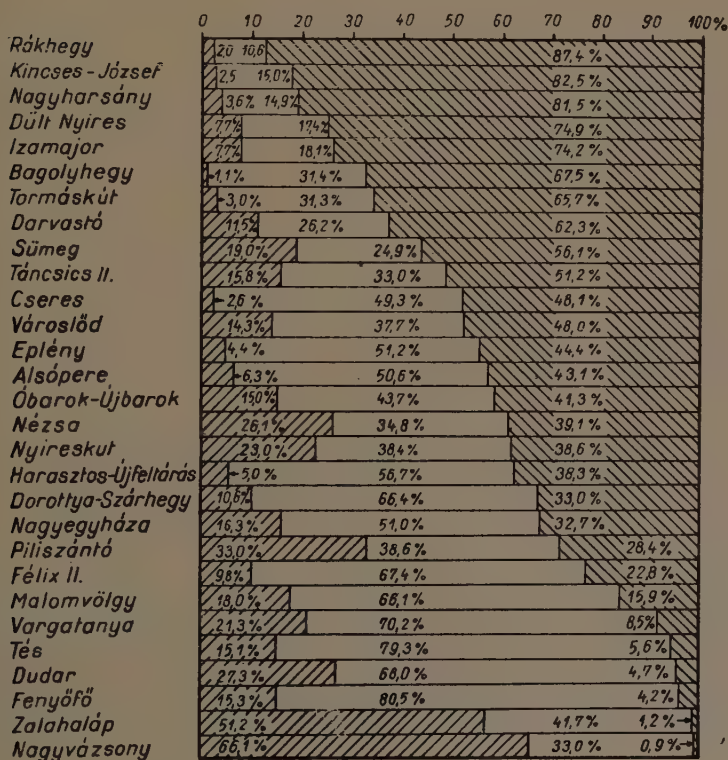


Fig. 3. Frequency distribution of Al<sub>2</sub>O<sub>3</sub> content

13,4%: frequency percentages of the three groups

occurrences are exceptions, however, the share of bauxitic clay being 57,1 and 66,1 per cent, respectively. Consequently, these have to be considered not so much as bauxite deposits but rather bauxitic clay occurrences containing a lot of argillaceous and some pure bauxite.

The frequency distribution is the most strikingly revealed by the frequency histograms constructed from the distribution tables. For this reason for each locality we have drawn the frequency histogram of alumina content. From the shape of the histograms, the localities can be graded into four groups (Diagram 1).

1. The shape of the histogram reflects the "ideal" composition of a homogeneous rock. It has a single symmetrical peak, i. e. the frequency percentages decrease both ways similarly.

Of the considered 29 localities 16 belong to this group (Zalahaláp, Vargatanya, Félix II, Dorottya-Szárhegy, Malomvölgy, Nagyvázsony, Cseres,

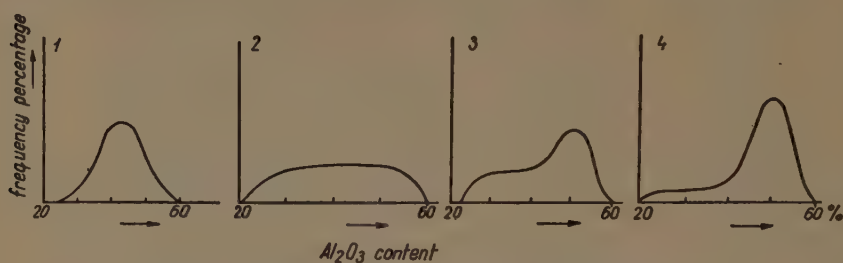


Diagram 1. Typical frequency diagrams of  $\text{Al}_2\text{O}_3$  content

Tormáskút, Fenyőfő, Dudar, Eplény, Alsópere, Tés, Bagolyhegy, Harasztos, Óbarok-Újbarok).

2. The histogram is squat with an unclearly defined peak, or with no peak at all. Notwithstanding, the distribution is symmetrical. There are five occurrences to this group (Pilisszántó, Táncsics II, Nagyegyháza, Nézsa and Városlőd). In these occurrences there is no excessive domination of any of the three rock types.

3. The asymmetry of the histogram is the outstanding feature of the third type. The peak occurs in the zone of large alumina percentages with somewhat smaller volumes of rock containing intermediate and small percentages of  $\text{Al}_2\text{O}_3$ . There are three occurrences of this sort (Nagyharsány, Nyíreskút and Sümeg).

4. This group is characterized by curves of a strong peak around 50 to 60 per cent and a flank with small amplitudes between 30 and 50 per cent. Towards the upper limit of alumina content the curve quite abruptly ceases. This type is the extremely asymmetric variety of the last one.

The occurrences of Nyirád: Izamajor, Dült-Nyíres and Darvastó as well as the Rákhegy and Kincses-József fields of Iszkaszentgyörgy can be relegated to this same group.

On comparing the above-defined groups with Table 2 of average alumina content it can easily be perceived that the histograms of occurrences of



small average alumina content are more similar to the ideal homogeneous rock composition. It seems that bauxitization of the present locality had a material as a base of such a composition. Already this, somewhat bauxitized material, could have been transported from elsewhere. On the other hand, the histograms of occurrences with the largest averages tend to be most askew, namely in the direction of large alumina content. The inverse sort of asymmetry was not observed in any of the cases. In our opinion this feature is likewise connected with the one-directional character of the bauxitization process. This is why the end product of the process was most accumulated, resulting in the skewness of the distribution. The drawn-out flank was probably left over by a natural slowing-down of the bauxitization process, according to mass action law.

The absence of important cases of opposite skewness points to the absence of opposite (clay-forming) processes of notable intensity. However, the prevalence of the arithmetic mean over median and mode in cases of smaller average alumina content suggest the smaller-scale acting of such processes. The detailed explanation of this complex of problems will follow in the chapter on bauxite genetics, to be published in a separate paper.

Let us further investigate the scatter of the analysis data, i. e. the deviation of individual analyses from the arithmetic mean of the occurrence. Scatter may be expressed with the aid of two parameters, namely variance (average of square deviation) and standard deviation (square root of variance).\*

From a geochemical point of view these parameters indicate the deviation of the bauxite body from homogeneity, as regards the distribution of element or compound in question. In case of ideally homogeneous composition these parameters become infinitely small, whereas they will increase with the inhomogeneity of the rock body.

Variance and standard deviation were only computed for localities with a sufficient number of analyses, permitting a reliable determination. In case of too small a number of analyses the values tend to be overmuch influenced by exceptional analysis results.

The results are listed in Table 1. The standard deviation varies between rather broad limits (8,6—4,8 per cent). It is the smallest for the Kincses-József and Rákhegy occurrences (4,8 and 5,1). These localities possess the most

\*Variance is calculated by the formula

$$\delta^2 = \frac{\sum_1^n (x_i - x_0)^2 w_i}{\sum_1^n w_i}$$

where  $n$  is the number of non-empty statistical classes,  $x_i$  the percentage of alumina in the  $i^{\text{th}}$  analysis,  $x_0$  the value of the arithmetic mean and  $w$  the frequency of analyses in the individual classes.

The standard deviation is the square root of variance ( $\delta$ ).

homogeneous alumina distribution. The greatest scatter is observed at the occurrence of Táncsics II, standard deviation being almost twice the above value (8,6 per cent). The Táncsics II occurrence is a partly redeposited bauxite body covered by Miocene sediments. During redeposition the bauxite body underwent some inhomogenization. There are similarly great values of scatter, in all localities covered by sediments newer than Eocene, where there was a possibility of partial or complete reworking. Occurrences of this type are Óbarok-Újbarok (7,4 per cent), Darvastó (7,2 per cent) and Nagygyháza (6,9 per cent). From this point of view the great variance and standard deviation characterizing the Eocene-covered i. e. unreworkeed Izamajor, Dült-Nyíres and Városlőd fields seem peculiar. However, the excessive asymmetry of the distribution mentioned is sufficient explanation for so great a scatter.

To study the geographical distribution of alumina accumulation, the true average alumina content of the occurrences, obtained by correcting for accessories and traces, was plotted on a condensed geologic map of the Transdanubian Central Hungarian Mountains (Fig. 4). According to this figure, the occurrences with maximum alumina content occur along a line of NE-SW strike, on both sides bordered by areas with localities of less than 40 per cent average alumina content. The optimal zone of bauxite formation is some ten kilometres wide. It exhibits two soft archings of a southeasterly trend, one around Nyirád and Halimba and an other around Iszkaszentgyörgy and Gánt. It is just at these points that alumina content reaches peak values (above 46 per cent).

In the Bakony Mountains the average alumina content of occurrences lying North and South of the optimal axis inversely varies with the distance of the occurrence from the same. E. g. we find this feature proceeding from Halimba through the Szőc fields towards Nagyvázsony as well as, considering the Zalahaláp occurrence and the Tés, Dudar and Fenyőfő localities. Moreover, the same relation holds true for the Buda-Pilis Mountains, as proven by the Pilisszántó, Pilisvörösvár, Budakeszi sequence of occurrences. The bauxite boulders found in the area of Szentkirályszabadja were most probably transported in the lower Pliocene from the NW, this being the reason for their anomalously high alumina content (41,1 per cent).

According to the generally accepted view, all of Hungarian bauxite deposits have originally been of the same high quality, which was subsequently degraded by chemical processes (Dudar) or by redeposition and resilification (Zalahaláp, Öcs). This view is herewith proved untenable, as more or less redeposited bauxite bodies of relatively young cover (Táncsics II, Eplény, Óbarok-Újbarok, Nagygyháza) are seen to occur along the optimum axis.

According to our opinion, the evolution of this bauxite axis may most probably be due to palaeogeographic reasons. However, the detailed palaeogeographic maps of the individual Cretaceous stages which would more



easily facilitate the discussion of this point are as yet lacking. Nevertheless, it suggests itself that the zone of the bauxite axis must have been a peneplained flatland on the shore of the Cretaceous sea.

The sketch map above given, will be useful in planning perspective bauxite prospecting, as it points out the areas which seem the most hopeful.

Finally, we have to discuss the Nagyarsány deposit, geographically as geochemically separated from the rest of our bauxite occurrences. Its alumina content (56,7 per cent on the average) is significantly exceeding that of the others. The explanation for this feature may lie in differences of mother rock as well as in the different circumstances of formation.

In looking for a correspondence between the geological age and the alumina content in Table 2 we have listed the geological age of the immediate cover of the bauxite deposits. The compilation shows that in occurrences with lower and upper Cretaceous or Eocene cover there is no correlation between alumina content and cover age. Consequently, alumina accumulation was controlled by the palaeogeographic situation rather than by the stratigraphic position.

The deposits carrying Oligocene or younger covers may also be of relatively greater (Darvastó, Táncsics II, Eplény) or smaller (Zalahaláp, Nagyvázsöny) alumina content. As the post-depositional geological history of these deposits must have been much more eventful than that of the above ones, it is remarkable that the chemical composition should be so much less influenced than hitherto supposed. Therefore the bauxite deposits rather suffered total erosion, than degradation.

### *Silica content of bauxite*

An overwhelming majority (99 per cent) of silica in bauxite occurs in the form of clay minerals. Quartz is totally negligible in most of the occurrences. Silica content may greatly vary within the bauxite complex, extremities of 0,1 and 55 per cent being possible. We have treated the data of silica content in the same manner as those of alumina. The maximum and minimum values of the individual occurrences are similarly listed (Table 3). The 0,5 per cent minimum is quite frequent, it occurs in most of the fields around Nyirád, Halimba, Szóc and Iszkaszentgyörgy. In most of the other localities it ranges from 1 to 5 per cent, reaching 8 to 14 per cent in no more than five small occurrences (Zalahaláp, Nagyvázsöny, Fenyőfő, Dudar, Tés). The small extremes for most of the fields above-noted are not exceptional values. By excluding one per cent of the analyses the lower limit is increased by but 0,5 to 2,0 per cent.

On the other hand, there are a number of exceptional values around the upper extreme. The greatest silica content was observed in one of the Malom-völgy samples (55 per cent). In all of the other occurrences the maximum ranged

Table 3

Geochemical parameters of  $\text{SiO}_2$  content

Occurrence	Extremals				Central values			Scatter	
	lower		upper		Arith- metic mean	Median	Mode	Variance	Standard devia- tion
	100%	99%	99%	100%					
Sümeg .....	1,0	2,0	44,0	46,0	17,2	12,3	2,5		
Nyirád : Darvastó .....	0,1	1,0	40,0	44,0	11,5	5,6	2,5	135,7	$\pm 11,6$
„ Deákihegy .....	0,1	0,5	39,0	41,0	11,0	6,2	1,5	122,9	$\pm 11,1$
„ Táncsics II. ....	0,1	0,5	39,5	42,0	17,6	16,1	2,5	145,1	$\pm 12,0$
„ Izamajor .....	0,1	1,0	41,5	46,0	11,8	6,4	2,5	141,5	$\pm 11,9$
Zalahaláp .....	14,0	17,5	43,5	46,0	35,3	36,7	36,5		
Szőc : Vargatanya .....	5,0	6,0	38,0	39,0	22,8	22,3	17,5		
„ Félix II. ....	0,1	1,5	39,0	40,0	19,5	20,0	26,5	87,7	$\pm 9,4$
„ Dorottya—Szárhegy	0,1	1,0	39,5	42,0	13,7	12,4	2,5	111,9	$\pm 10,6$
„ Nyíreskút .....	1,0	1,5	40,5	42,0	16,9	13,3	4,5		
„ Malomvölgy .....	1,0	1,0	43,0	55,0	18,1	18,6	2,5	121,3	$\pm 11,0$
Nagyvázsony .....	9,0	13,5	43,5	45,0	33,8	35,9	36,5		
Halimba : Cseres .....	0,1	0,5	38,0	43,0	16,3	17,1	1,5	95,0	$\pm 9,7$
„ Tormáskút .....	0,1	0,5	35,0	49,0	12,7	11,0	1,5	68,9	$\pm 8,3$
Városlőd : Öreghegy .....	1,0	1,0	39,5	47,0	18,2	16,7	9,5	127,3	$\pm 11,3$
Fenyőfő .....	11,0	13,0	43,0	44,0	30,0	29,9	30,5 (28,5)		
Dudar .....	8,0	10,5	40,0	41,0	27,8	27,0	25,5		
Eplény .....	1,0	2,5	34,5	40,0	14,0	12,6	4,5		
Alsópere .....	2,0	2,0	38,0	41,0	18,3	18,8	21,5	70,3	$\pm 8,4$
Tés .....	14,0	17,0	37,0	38,0	25,0	24,4	23,5		
Iszka-szentgyörgy									
Kincses-József	0,1	1,0	36,5	44,0	8,2	6,0	2,5	49,2	$\pm 7,0$
„ Rákhegy .....	0,1	1,0	36,0	39,0	8,0	4,8	1,5	63,5	$\pm 8,0$
Gánt : Bagolyhegy .....	1,0	3,0	37,0	42,0	16,5	16,0	14,5	54,8	$\pm 7,4$
„ Harasztos, Meleges, Újfeltárás .....	1,0	3,0	41,0	46,0	21,1	21,2	27,5	83,7	$\pm 9,1$
Óbarok—Újbarok— Vázsony psz. ....	2,0	4,0	41,5	47,0	17,3	13,7	9,5	114,4	$\pm 10,7$
Nagyegyháza .....	3,0	4,0	41,0	46,0	19,9	18,7	11,5	108,6	$\pm 10,4$
Pilis-zántó .....	3,0	3,5	44,0	45,0	21,7	20,7	20,5		
Nézsza .....	1,0	1,0	45,0	46,0	22,5	26,5	1,5		
Nagyharsány .....	0,1	0,5	45,0	52,0	15,0	9,3	4,5		

from 38 to 49 per cent. However, after excluding the lateral one per cent the extremes were reduced by as much as 4 to 8 per cent, indicating that no more than a negligible part of the bauxite body is composed of rocks of an excessive



Table 4

*Comparison of average SiO<sub>2</sub> content with other characteristic parameters*

Occurrence	Arithmetic mean	Difference		Age of immediate cover	Shape of histogram
		to median	to mode		
Rákhegy	8,0	- 3,2	- 6,5	1. Eocene	
Kincses-József	8,2	- 2,0	- 5,7	1. Eocene	
Deákihegy	11,0	- 4,8	- 9,5	1. Eocene	
Darvastó	11,5	- 5,9	- 9,0	Pleistocene+ 1. Eocene	
Izamajor	11,8	- 5,4	- 9,3	1. Eocene	
Tormáskút	12,7	- 1,7	-11,2	Turonian	
Dorottya-Szárhegy	13,7	- 1,3	-11,2	1. Eocene	
Eplény	14,0	- 1,4	- 9,5	Pleistocene+ 1. Eocene	
Nagyharsány	15,0	- 5,7	-10,5	Aptian	
Cseres	16,3	+ 0,8	-14,8	1. Eocene	
Bagolyhegy	16,5	- 0,5	- 2,0	1. Eocene	
Nyíreskút	16,9	- 3,6	-12,4	1. Pliocene + 1. Eocene	
Sümeg	17,2	- 4,9	-14,7	m.Eocene	
Óbarok-Ujbarok	17,3	- 3,6	- 7,8	u.Oligocene	
Táncsics II	17,6	- 1,5	-15,1	Tortonian	
Malomvölgy	18,1	+ 0,5	-15,6	1. Eocene	
Városlód	18,2	- 1,5	- 8,7	1. Eocene	
Alsópere	18,3	+ 0,5	+ 3,2	Aptian	
Harasztos - Ujfeltárás	18,3			1. Eocene	
Félix II	19,5	+ 0,5	+ 7,0	1. Eocene	
Nagyegyháza	19,9	- 1,2	- 8,4	u.Oligocene	
Pilisszántó	21,7	- 1,0	- 1,2	1. Eocene	
Nézsza	22,5	+ 4,0	-21,0	m.Eocene	
Vargatanya	22,8	- 0,5	- 5,3	1. Eocene	
Tés	25,0	- 0,6	- 1,5	Aptian	
Dudar	27,8	- 0,8	- 2,3	1. Eocene	
Fenyőfű	30,0	- 0,1	+ 0,5	1. Eocene	
Nagyvázsony	33,8	+ 2,1	+ 2,7	Pliocene	
Zalahaláp	35,3	+ 1,4	+ 1,2	Tortonian	

silica content. The maximum ranges to be regarded as valid are from 37 to 43 per cent.

The arithmetic mean silica content of bauxite occurrences is rather variable : a minimum of 8,0 per cent was found for Rákhegy and a maximum of 35,3 for Zalahaláp (Table 4). In the bulk of occurrences, however, the mean lies between 15 and 25 per cent. In average the great differences of silica content point to the fact that of the main components, silica has suffered the most important geochemical influences.

On the basis of arithmetic mean computation the average silica content of Hungarian bauxite was found to be 18,0 per cent. This value is remarkably great : however, we must consider that the geological bauxite bodies here treated consist to some part not only of pure bauxite. Thus the average rock of the bauxite body in nature reveals itself to be rather argillaceous.

The frequency distribution of silica is the most asymmetric of all of the main components. Consequently, in most cases there is a marked difference between medians and arithmetic means. The differences are listed in Table 4, similarly to those computed for alumina. The picture is roughly the opposite of that obtained for the latter. The median is in most cases smaller than the arithmetic mean, excepting some localities of large silica content. In bauxite, silica is an exact opposite to alumina : the enrichment of the one is accompanied by a poverty in the other. On the other hand, the differences between arithmetic mean and median are greater than in the case of alumina (2 to 6 per cent).

The behavior of the mode is of special interest. In 12 of the occurrences the mode, i. e. the most frequent silica percentage, varies from 1,0 to 3,0 per cent. This group contains all the fields around Nyirád, Iszkaszentgyörgy and Halimba as well as Dorottya-Szárhegy at Szőc and Nézsa. In these localities the most frequent silica percentage is by far (7 to 20 per cent) smaller than the arithmetic mean. This indicates that in these localities pure bauxite with almost no silica is predominant. In localities with greater silica averages the difference tends to be much smaller. Also here the mode is generally less than the arithmetic mean. However, especially at occurrences of maximum silica content, the mode exceeds the arithmetic mean (Zalahaláp, Nagyvázsony, Fenyőfő).

The large negative skewness observed throughout the silica distributions indicate that in the course of bauxitization this element suffered one-directional changes the most intensely (extraction, washing-out, desilification). The simultaneous enrichment of aluminium, iron and titanium have occurred at the expenses of this single element.

Also here frequency percentages were relegated into the three following groups :

1.  $\text{SiO}_2$  content below 10 per cent;
2.  $\text{SiO}_2$  content 10 to 30 per cent;
3.  $\text{SiO}_2$  content above 30 per cent.







This classification is arbitrary to some extent. It rests on the practical usage of calling bauxite silica-poor if containing less than ten per cent silica and silica-rich if containing more than thirty.

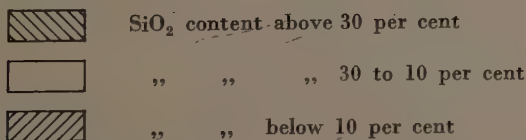
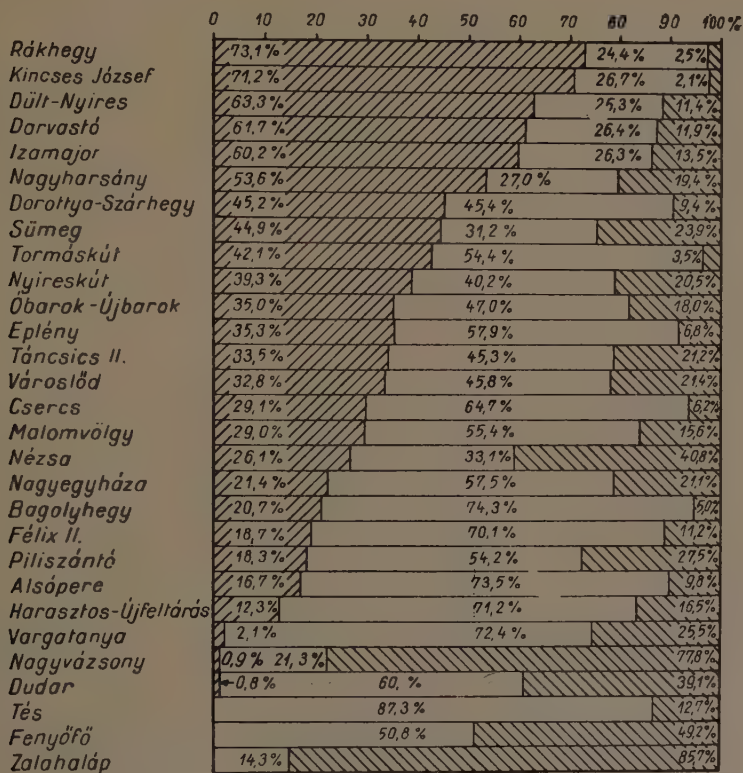


Fig. 5. Frequency distribution of SiO<sub>2</sub> content

12.3% : frequency percentages of the three groups

The predominance of silica-poor bauxite (73.1 per cent) is conspicuous in the case of the Rákhegy occurrence. It occurs in similarly great quantities in the Kincses-József, Dült-Nyíres, Darvastó and Izamajor deposits (71 to 60 per cent). The Iszkaszentgyörgy region consequently contains the purest bauxite of our country, a fact that was already demonstrated by the arithmetic means (Fig. 5).



The subsequent group contains eighteen occurrences. With the exception of some smaller localities they belong to the Halimbà, Gánt and Szőc areas. In these, the silica-poor and intermediate types occur in approximately equal proportions, whereas some are even characterized by the predominance of the latter (Alsópere 73,5, Bagolyhegy 74,3, Harasztos 71,2 per cent).

In the occurrences of the Halimba and Gánt environment the share of silica-rich (clayey) bauxite does not yet exceed 10 per cent, but in the others it reaches to as much as to 30 to 40 per cent.

The last group contains six occurrences of smaller sizes. In these the proportion of bauxite containing less than 10 per cent silica is insignificant

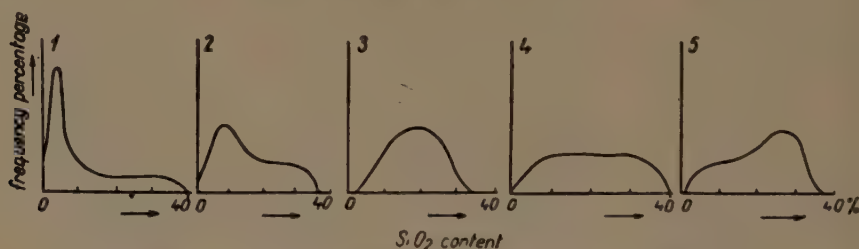


Diagram 2. Typical frequency diagrams of  $\text{SiO}_2$  content

(less than 2 per cent) or equalling zero. Four of these (Vargatanya, Dudar, Tés, Fenyőfő) mostly consist of the intermediate type, whereas the remaining two (Zalahaláp and Nagyvázsöny) are characterized by a predominance of the clayey sort (77,8 and 85,7 per cent, respectively). These two occurrences also showed the greatest averages in silica content.

The shape of the frequency histograms essentially differs from those of the alumina distribution. They can be divided into five groups.

1. The first group contains two localities of the Iszkaszentgyörgy and two of the Nyirád neighbourhood, all of these are primary ones. The histograms are characterized by excessive skewness. An enormous peak occurs between 1 and 4 per cents of silica content, maximum frequencies reaching 16 to 18 per cent. At higher percentages the peak rather sharply falls off and continues up to 40 to 45 per cent silica content with amplitudes of 1 to 3 per cent.

This distribution indicates that in the five occurrences listed above the predominant, i. e. characteristic part of the bauxite body consists of bauxite very poor in silica, accompanied by types of extremely variably silica content. However, there is no intermediate or silica-rich type accumulated, as much as to form another peak.

2. The histogram of the second group is of a similar nature, with a less pronounced skewness, smaller peak and better-developed (3 to 5 per cent) high-percentage wing. There are nine occurrences in this group, viz. Dorottya-

Szárhegy, Tormáskút, Tánecsics-II, Óbarok-Újbarok, Cseres, Eplény, Nagyharsány, Nyíreskút, Sümeg.

3. The third group contains eight localities. (Vargatanya, Dudar, Fenyőfő Alsópere, Tés, Bagolyhegy, Harasztos, Félix II.) Common features of their histograms are a single peak and approximate symmetry. The closest to an ideal homogeneous rock composition are the histograms of the Bagolyhegy and Harasztos-Újfeltárás localities. In the others the general course of the histogram is disturbed by exceptional local frequency values. In our opinion these out-jutting values are not due to geochemical agencies, but rather to the small number of analyses available from these occurrences. There is a greater weight to exceptional values if the number of analyses is small.

The histograms indicate that, from the point of view of silica content, homogeneity of rock is the most closely approached by the bauxite of this type.

4. There are five occurrences in this group (Malomvölgy, Városlőd, Nagyegyháza, Pilisszántó, Nézsa). The histogram is likewise symmetric but the peak is less sharp or even lacking. In these localities the distribution of silica is most heterogeneous: there is no characteristic accumulation of any type, except irregularly placed (local) partial peaks.

5. In the fifth group the histogram is approximately the opposite of the asymmetric second group. The localities pertaining to this group are Nagyvázsöny and Zalahaláp: this is where the bauxite complex mostly consists of bauxitic clay or argillaceous bauxite with only small amounts of typical bauxite of intermediate or small silica content.

In correlating the histogram types with the amplitudes of average silica content (Table 4), an interesting relationship is shown. It is found that the histograms of occurrences poorest in silica are the farthest from symmetry, the skewness being towards small silica percentages (Group 1). The histograms of the less asymmetric second group next follow. The histograms of occurrences of intermediate and great silica content are symmetrical (Groups 4 and 5), whereas in the two localities of maximum silica content (Group 5) there is an inverse skewness.

This regularity can be explained, similarly to the one found for alumina, by the nature of the bauxitization process. In our opinion the prevalence of small silica content rocks and the corresponding asymmetry of the distribution was brought about by the irreversibility of bauxitization. The more intense the bauxitization, the more expressive is the asymmetry.

The inverse skewness observed in the case of the two occurrences of the greatest silica content, points to some kind of resilification that was caused not so much by the emigration of alumina as by the immigration of silica. This statement is based on the normality of alumina histograms of these localities.

Variance and standard deviation were likewise only computed to  $\text{Al}_2\text{O}_3$  for occurrences with a sufficient number of analyses (Table 3). The scatter of silica percentages is much greater than was found for alumina. In comparison to the average variance of alumina for Hungarian occurrences (45,0), that of silica amounts to 100,1. Variance itself varies rather greatly (49,0 to 145,1 or, expressed in standard deviation, 7,0 to 12,0 per cent).

Scatter is the smallest in the Kincses-József field (49,2 by variance and 7,0 by standard deviation). A similarly small scatter is observed at the other field of the Iszkaszentgyörgy area (Rákhegy) as well as at the occurrences of the Halimba and Gánt environment (standard deviation being 7 to 10 per cent). Surprisingly, great scatter occurs at the Nyirád fields, reaching the highest at the Tánácsics II locality (variance : 145,1 standard deviation : 12,0 per cent). This intense scatter can be explained by the secondary, redeposited nature of this occurrence, as it is a matter of course that the formerly homogeneous rock should have suffered a lot of irregular changes in the course of redeposition. On the other hand, the great scatter on the three other fields of the Nyirád region, where deposition is primary, can be due to the great skewness of the distribution. The relatively great scatter at the Városlőd, Malomvölgy and Dorottya-Szárhegy deposits (standard deviation reaching 10,6 to 11,3 per cent) can be explained in a similar way. The scatter is greater at the Nagyegyháza and Óbarok-Újbarok occurrences too. This feature is due to the secondary position of bauxite.

By plotting the areal distribution and geological position of average silica percentages, a picture very much resembling the inverse of the alumina map is obtained (Fig. 6). On connecting the occurrences of the smallest silica content, a line is obtained which strikes one in just the way as the maximum line of alumina. Along this line the smallest silica content is encountered at the Nyirád and Iszkaszentgyörgy areas. These lie, similarly to alumina maxima, in the two archings of the line. Between the two minima, along the line, there is an increase of silica percentage to 18, whereas perpendicularly to the line, values of 30 to 35 per cent are reached in both ways. Northeast of Iszkaszentgyörgy there is likewise an increase of silica content along the line, reaching maximum at the lateral occurrence of Nézsa (22,5 per cent).

Looking at the silica percentages from the stratigraphical point of view, we can see that the average content of occurrences with Lower Cretaceous cover is not much different from those with Upper Cretaceous or Eocene cover. (See Table 4.) In all of the three types localities occur of small, intermediate and large silica content.

Among the occurrences with Oligocene to Pleistocene cover there are similarly those of small silica content (Darvastó, Eplény) : however, they are mostly characterized by intermediate or large silica percentages. Consequently, it may be stated that in the course of the erosion of bauxite deposits there



occurred a certain amount of degradation (resilification) of varying intensity. However, this resilification could by far not be as intense as was generally supposed hitherto.

### *Iron content of bauxite*

Its amount is given by the analyses in the form of ferric oxide, although bauxite invariably contains smaller or greater amounts of ferrous iron as well. Because of this we were constrained in carrying out our calculations with the ferric oxide percentages. It should be, however, stressed that the data refer to total iron content, as ferrous iron is oxidized and incorporated into the ferric iron percentage.

Analyses which separately give ferrous and ferric iron content are scarce. These will be concisely evaluated at the end of this chapter.

Iron content within the bauxite body is also subjected to rather intense variations. There are samples containing almost no iron, while at some points enrichment over 50 per cent of ferric oxide may occur. In the latter case the rock in question can be termed a sedimentary ferrillite, much rather than an allitic one.

The extremals of iron content were tabulated exactly in the same way as those of alumina and silica. The extremals obtained after excluding the lateral one per cent of analyses on both sides were also computed (see Table 5).

There are two occurrences (Izamajor and Bagolyhegy) containing some bauxite which almost totally lack iron. In the remainder minimum iron content generally varies from 1 to 4 per cent. There are only two exceptions, namely Nyíreskút and Tés, with 7 and 8 per cent, respectively. However, with most of the occurrences very small minima proved to be exceptional. After eliminating the lateral one per cent of analyses, minimum iron content was shifted from 4 to 8 per cent.

The greatest percentage, 56,0, was found in one sample of the Kincses-József field. In the others the maximum ranges from 35 to 50 per cent. Exceptions are the Zalahaláp, Nagyvázsöny and Nagyharsány fields where bauxites above 29 and 25 per cent, respectively of iron oxide are, unknown. On excluding the lateral one per cent, the extremals generally sink to 30–35 per cent, indicating that rocks above this value form but a negligibly small part of the bauxite body.

The arithmetic mean of the particular occurrences ranges between 8 and 23 per cent. Peak value occurs at Tormáskút (22,7 per cent). Otherwise with most of the localities (20 of them) it lies between 16 and 20 per cent. To this group belong, among others, the occurrences of the Halimba, Nyirád and Iszka-szentgyörgy areas. At the localities Dudar, Fenyőfő, Zalahaláp and Nagy-

Table 5  
Geochemical parameters of  $Fe_2O_3$  content

Occurrence	Extremals				Central values			Scatter	
	lower		upper		Arith- metic mean	Median	Mode	Vari- ance	Stan- dard deviation
	100%	99%	99%	100%					
Sümeg .....	3,0	4,0	38,0	48,0	19,5	20,7	24,5		
Nyírad: Darvastó .....	1,0	4,5	30,5	41,0	20,1	22,0	23,5	34,7	$\pm 5,9$
„ Deákihegy .....	3,0	7,5	30,0	36,0	21,5	23,2	24,5	28,7	$\pm 5,4$
„ Táncsics II. ....	3,0	6,5	30,5	34,0	19,8	20,8	21,5	33,2	$\pm 5,8$
„ Izamajor .....	0,0	3,5	33,5	51,0	21,5	23,5	24,5	43,0	$\pm 6,6$
Zalahaláp .....	2,0	5,5	25,5	29,0	13,2	12,6	10,5		
Szőc: Vargatanya .....	2,0	4,0	31,5	32,0	16,7	16,8	17,5		
„ Félix II. ....	3,0	5,5	27,5	33,0	17,5	17,4	16,5	17,2	$\pm 4,2$
„ Dorottya—Szárhegy	2,0	6,5	38,0	49,0	20,3	20,4	21,5	26,4	$\pm 5,1$
„ Nyíreskút .....	7,0	9,0	32,0	38,0	20,4	20,6	20,5		
„ Malomvölgy .....	1,0	3,0	37,0	45,0	19,9	19,6	18,5	29,3	$\pm 5,4$
Nagyvázsony .....	4,0	6,0	24,5	26,0	14,4	14,2	14,5		
Halimba: Cseres .....	4,0	8,5	31,0	44,0	20,1	20,0	19,5	20,5	$\pm 4,5$
„ Tormáskút .....	1,0	10,5	35,5	51,0	22,7	22,4	21,5	24,9	$\pm 5,0$
Városlőd: Öreghegy .....	4,0	8,0	30,5	37,0	19,3	19,5	19,5	20,0	$\pm 4,5$
Fenyőfő .....	4,0	5,5	29,5	38,0	13,4	13,7	13,5		
Dudar .....	3,0	3,5	32,5	36,0	14,4	13,6	10,5		
Eplény .....	5,0	7,5	29,5	38,0	19,9	20,3	21,5		
Alsópere .....	2,0	3,0	30,0	35,0	17,9	18,9	19,5	31,4	$\pm 5,6$
Tés.....	8,0	9,0	36,5	44,0	19,7	19,4	19,5		
Iszkaszentgyörgy:									
Kincses-József	2,0	6,5	35,5	56,0	18,8	19,4	20,5	23,9	$\pm 4,9$
„ Rákhegy .....	4,0	8,0	27,5	52,0	20,3	21,4	22,5	18,3	$\pm 4,3$
Gánt: Bagolyhegy .....	0,0	6,0	32,5	40,0	16,2	15,4	14,5	28,0	$\pm 5,3$
„ Harasztos, Meleges, Újfeltárás .....	3,0	5,0	31,5	41,0	16,1	15,3	12,5	32,3	$\pm 5,7$
Óbarok—Újbarok— Vázsony psz. ....	2,0	4,0	33,0	44,0	18,1	18,2	17,5	35,7	$\pm 6,0$
Nagygyháza .....	2,0	4,0	33,0	40,0	18,0	17,9	16,5	37,3	$\pm 6,1$
Piliszsántó .....	1,3	3,0	46,0	47,0	21,9	22,4	23,5		
Nézsa .....	1,0	2,0	29,0	31,0	17,3	17,3	24,5		
Nagyharsány .....	1,0	1,0	24,5	25,0	9,2	7,9	4,5		

vázsony mean ferric oxide content is 13 to 14 per cent. It reaches minimum at Nagyharsány with an arithmetic mean percentage of 9,2.

The iron oxide content of average Hungarian bauxite was computed to be 18,8 per cent.

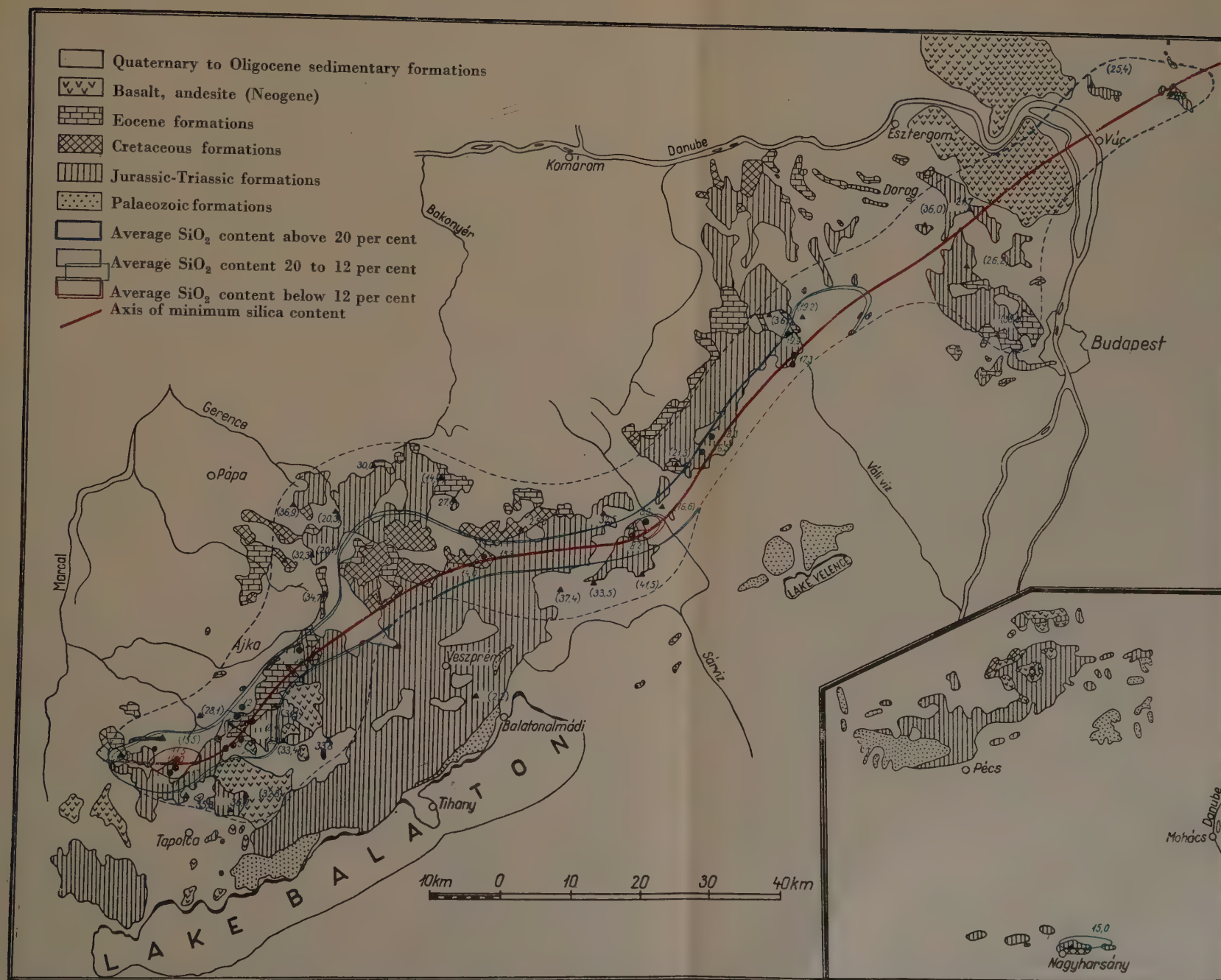


Fig. 6. Average  $\text{SiO}_2$  content of Hungarian bauxite occurrences

● Larger, thoroughly investigated occurrences

▲ Smaller, less thoroughly known occurrences and superficial indications

46.9 Average silica content of occurrence






























(36.0) Uncertain average from small number of data





Table 6

*Comparison of average  $Fe_2O_3$  content with other characteristic parameters*

Occurrence	Arithmetic mean	Difference		Age of immediate cover	Shape of histogram
		to median	to mode		
Tormáskút	22,7	- 0,3	- 1,2	Turonian	
Pilisszántó	21,9	+ 0,5	+ 1,6	l.Eocene	
Izamajor	21,5	+ 2,0	+ 3,0	l.Eocene	
Deákihegy	21,5	+ 1,7	+ 3,0	l.Eocene	
Nyireskút	20,4	+ 0,2	+ 0,1	l.Pliocene + l.Eocene	
Rákhegy	20,3	+ 1,1	+ 2,2	l.Eocene	
Dorottya-Szárhegy	20,3	+ 0,1	+ 1,2	l.Eocene	
Cseres	20,1	- 0,1	- 0,6	l.Eocene	
Darvastó	20,1	+ 1,9	+ 3,4	Pleistocene + l.Eocene	
Eplény	19,9	+ 0,4	+ 1,6	Pleistocene + l.Eocene	
Malomvölgy	19,9	- 0,3	- 1,4	l.Eocene	
Táncsics II	19,8	+ 1,0	+ 1,7	Tortonian	
Tés	19,7	- 0,3	- 0,2	Aptian	
Sümeg	19,5	+ 1,2	+ 5,0	m.Eocene	
Városlőd	19,3	+ 0,2	+ 0,2	l.Eocene	
Kincses-József	18,8	+ 0,6	+ 1,7	l.Eocene	
Óbarok-Ujbarok	18,1	+ 0,1	- 0,6	u.Oligocene	
Nagygyháza	18,0	- 0,1	- 1,5	u.Oligocene	
Alsópere	17,9	+ 1,0	+ 1,6	Aptian	
Félix II	17,5	- 0,1	- 1,0	l.Eocene	
Nézsza	17,3	± 0,0	+ 7,2	m.Eocene	
Vargatanya	16,7	+ 0,1	+ 0,8	l.Eocene	
Harasztos-Ujfeltárás	16,7			l.Eocene	
Bagolyhegy	16,2	- 0,8	- 1,7	l.Eocene	
Dudar	14,4	- 0,8	- 3,9	l.Eocene	
Nagyvázsony	14,4	- 0,2	+ 0,1	Pliocene	
Fenyőfő	13,4	+ 0,3	+ 0,1	l.Eocene	
Zalahaláp	13,2	- 0,6	- 2,7	Tortonian	
Nagyharsány	9,2	- 1,3	- 4,7	Aptian	

The deviations of medians and modes from arithmetic means are much smaller than with alumina and silica (Table 6). The difference of arithmetic mean and median is generally below one per cent and does never exceed two. The difference from the mode is somewhat greater, 1 to 3 per cent on the average. Most of the differences are positive, thus showing a similarity to

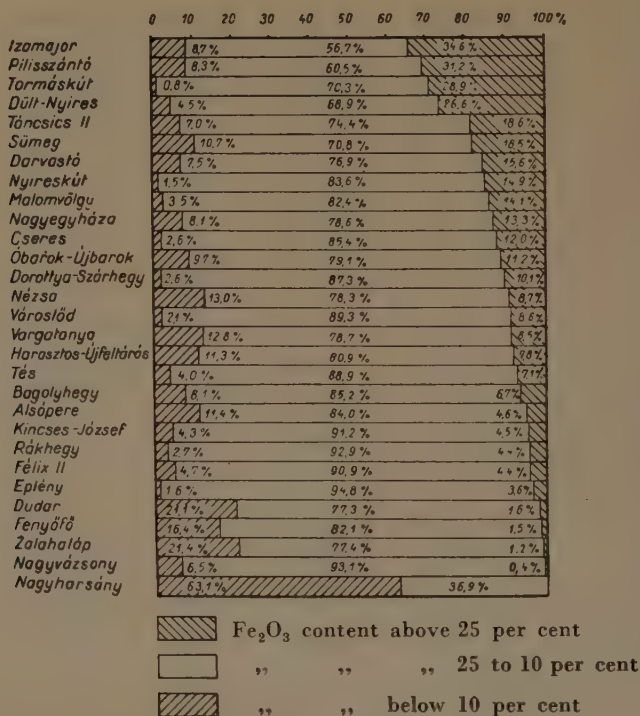


Fig. 7. Frequency distribution of  $\text{Fe}_2\text{O}_3$  content

15,6 : frequency percentages of the three groups

alumina. However, the relation between the intensity of concentration and the differences of central values there observed could not be demonstrated here, although there is an undeniable tendency towards it.

Consequently, of the three main elements so far treated the distribution of iron was revealed as the most symmetrical. Ideal homogeneous rock composition can best be approximated by bauxite in respect to this component.

Frequency percentages were also graded here into three groups, namely

1.  $\text{Fe}_2\text{O}_3$  content above 25 per cent ;
2.  $\text{Fe}_2\text{O}_3$  content 25 to 10 per cent ;
3.  $\text{Fe}_2\text{O}_3$  content below 10 per cent.



Like all subdivisions of this kind, this is also arbitrary to some extent. By the fact it can be supported that in industrial practice one distinguishes the iron-rich bauxite above 25 per cent, from iron-poor bauxite below ten per cent and in between of intermediate types (Fig. 7).

Most bauxite is of the intermediate kind in all the occurrences, forming 56,7 to 97,6 per cent of the deposit. The percentage of the intermediate kind is the greatest at the Eplény and Nagyvázsony deposits and at the two Iszka-szentgyörgy fields. The greatest amounts of iron-rich bauxite occur in Iza-major (34,6 per cent) and Pilisszántó (31,2 per cent). There is further a quite great lot of this kind in the Tormáskút (28,9 per cent) and Dült-Nyíres (26,6 per cent) deposits. In the remainder the frequency varies from 5 to 18 per cent.

Contrary to this, there are five occurrences at which the amount of iron-rich bauxite is practically negligible (0,0—1,6 per cent), namely the Dudar, Fenyőfő, Zalahaláp, Nagyvázsony and Nagyharsány ones. The greatest proportions of iron-poor bauxite are known to be from Nagyharsány (63,1 per cent), Dudar (21,1), Zalahaláp (21,4) and Fenyőfő (16,4), respectively. Otherwise the percentage of iron-poor bauxite is 2 to 10. The smallest amount of iron-poor bauxite can be noted in connection with the Tormáskút occurrence where it forms no more than 0,8 per cent of the deposit.

Consequently, Hungarian bauxite deposits consist in the most part of bauxite with intermediate iron content. Iron-rich bauxite is somewhat more frequent than the iron-poor, which latter only forms a negligible part of about 10 per cent of the deposits. From this point of view the Nagyharsány occurrence stands out sharply, totally lacking the iron-rich kind and consisting to an extent of 63,1 per cent of the intermediate one.

Knowledge of the role played by iron-rich and iron-poor varieties is also important for practical purposes, namely from the point of view of exploiting Hungarian bauxite as an iron ore. Another industrial importance for iron-poor bauxite lies in its use as a refractory. It is remarkable that the Tés bauxite, generally considered to be exceedingly iron-rich, even termed by some geologists "ferrobauxite ore", by our investigations was found to contain no more than 7,1 per cent of iron-rich bauxite, and which in reality belongs to the group of intermediate iron content.

The frequency histograms of the iron content of bauxite are much more homogeneous, with smaller deviations, than those of alumina and silica.

As to the shape of the histogram, we may distinguish four types, much less differing from each other than the types defined for alumina and silica (Diagram 3).

1st type. Most of the occurrences, 13 in number, belong to the first group (Városlőd, Nagyvázsony, Fenyőfő, Tés, Tormáskút, Nyíreskút, Dorottya-Szárhegy, Cseres, Malomvölgy, Óbarok-Újbarok, Nagyegyháza, Félix II, Vargatanya). Their histograms are entirely regular one-peak symmetrical

ones. Consequently, the iron distribution of these occurrences may be regarded as geochemically homogeneous.

2nd type. The second group contains two occurrences, the Pilisszántó and Nézsa ones. Their histograms are prolonged, with local peaks. All in all, these can also be considered as single-peak ones, because, of their completely symmetrical structure. The fact that these occurrences have only yielded a small number of analyses should be kept in mind. It is probable that on an increase of the number of analyses these partial maxima would fuse into a single central one.

3rd type. There are nine occurrences, namely Sümeg, Eplény, Alsópere and four of the Nyirád and two of the Iszkaszentgyörgy area, in the third

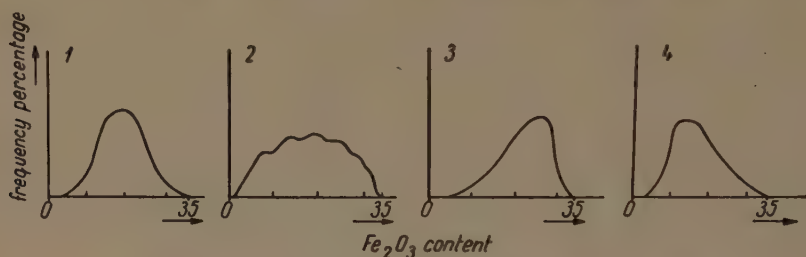


Diagram 3. Typical frequency diagrams of  $\text{Fe}_2\text{O}_3$  content

group. The histograms carry one slightly asymmetric peak which shifts towards greater iron percentages. At the Iszkaszentgyörgy fields the maxima are exceedingly sharp, peak frequency being 17 and 19 per cent, respectively, indicating the bulk of the bauxite body as being of identical iron content (19 to 22 per cent ferric oxide). The histograms show that, beside the intermediate kind, the amount of iron-poor bauxite is by no means negligible.

4th type. The five occurrences of the fourth group are Nagyharsány, Harasztos, Bagolyhegy, Dudar and Zalahaláp; their histograms are the opposite to those of the foregoing group, as the single peak is shifted towards smaller iron percentages. Neither is there a too great asymmetry.

It is to be seen in Table 6 that histograms of occurrences of low iron content are asymmetric in the direction of low iron percentages; on the contrary, those of high iron content show an asymmetry of opposite direction.

Symmetric histograms occur with great average iron contents as well as with smaller ones.

The asymmetries described may be due to oneway processes of iron accumulation or emigration.

On arranging the iron histograms in decreasing order of average alumina content, we find that the skewness of the iron histogram increases with it. Peak shifts towards greater percentages throughout also occurs with great alumina concentrations, indicating that bauxitization mostly goes together

with enrichment of iron. Although greater percentages of alumina can sometimes coincide with peak shifts to the opposite direction (Nagyharsány, Bagolyhegy, Harasztos). The explanation of this apparent contradiction will be dealt with in a following paper.

Variance and standard deviation were likewise computed for the greater occurrences. Results are listed in Table 5.

It can be observed that the scatter of iron content is much smaller than that of alumina and silica. The average variance of the studied localities amounts to 28,5 corresponding to a standard deviation of 5,3 per cent.

The scatters of the individual occurrences also exhibit smaller differences among themselves as was the case with the elements formerly treated. Maximum scatter occurs at the Izamajor locality, variance being 43,0, standard deviation, accordingly, 6,6 per cent. This is due to the skewness of the distribution.

A relatively large scatter also characterizes the Nagyegyháza and Óbarok-Újbarok occurrences (6,0 per cent standard deviation). This is easily explicable by the secondary, reworked nature of the deposits. The case is similar to the Darvastó and Táncsics II occurrences of the Nyirád area.

Scatter is somewhat less at the Halimba, Szőc and Iszkaszentgyörgy fields, indicating the homogeneity of iron distribution.

The average iron percentages above stated were correlated with the geographical distribution and geological position of the occurrences. The picture coincided, with the exception of some smaller features, from those obtained for alumina and silica. The line connecting localities of maximum percentage almost completely conforms to the former ones. However, this line has three points of maximum accumulation, namely the Nyirád-Halimba, Iszkaszentgyörgy and Pilisszántó areas. Average ferric oxide content is 20 to 22 per cent at these points (Fig. 8).

Each of these three foci are situated on the archings of the maximum line. The Nyirád-Halimba and Iszkaszentgyörgy-Gánt foci were already detected by analysis of the two foregoing components, whereas the Pilisszántó one only became obvious from the iron data. Along the main line there is an iron oxide content of 17 to 20 per cent between foci, only dropping below (16 per cent) at Gánt. In the Southwestern Bakony Mountains iron content gradually decreases with increasing distance from the maximum line: e.g. Tormáskút 22,7, Malomvölgy 19,9, Nagyvázsony 14,4 per cent. The same situation also prevails in the Northern Bakony: when leaving the line in a northerly direction we find Alsópere (17,9), Dudar (14,4), Fenyőfő (13,4 per cent).

Smallest iron content was found in localities lying the farthest off the main axis.

The coincidence of the accumulation areas of ferric oxide and alumina seems to indicate a similarity in behavior of these components in the course



of bauxitization. Consequently, iron is not a "contamination" in bauxite; on the contrary, it is an integral part of the complex of elements characterizing bauxite as a rock.

The Nagyharsány locality stands apart not only as regards geography but also in possessing a much smaller average ferric oxide content.

From the point of view of stratigraphy the picture is also similar to those obtained for alumina and silica: no direct relationship between cover age and chemical composition could be detected (Table 6).

The data on the ferrous iron content of our bauxite occurrences are relatively scarce. Up till now this was left undetermined not only by routine analyses, but also by so-called "total" analyses of fourteen components. We succeeded, however, in compiling 148 determinations for ferrous iron, 67 of which were obtained from the Bauxite Prospecting Firm; of the Ajka and Budapest laboratories, 4 were derived from the Gánt investigations of J. Kiss [4]; further 13 from analyses of the chemical laboratory of the Hungarian State Geological Institute; and the rest (64) with the courtesy of the Research Institute of Metal Industry, from their "bauxite file" under preparation. The individual localities — averages as determined from these 148 data are listed in Table 12.

The data given in this table do not comprise values for so-called grey pyritic-marcasitic bauxite, occurring in most of the localities on top of the bauxite body, in a thickness of 0,5 to 1,5 metres. Larger quantities of this sort are found firstly at the two Iszkaszentgyörgy fields and at the Cseres field of Halimba. In case of greater percentages of pyrite and/or marcasite, separate determining of ferrous and ferric iron is rather difficult, so that there are very few data of this kind. The most reliable are those given by the Research Institute for Heavy Chemical Industry (NEVIKI) of Veszprém, where large average samples (several hundred kilograms) of Kincses and Cseres grey marcasitic bauxite were investigated during the years 1955 and '56. The analyses yielded the following results:

Iszkaszentgyörgy-Kincses				Fe <sub>2</sub> O <sub>3</sub>	FeO		
Sample No.	1	grey	marcasitic	bauxite	5,75	8,42	per cent
	2	"	"	"	5,43	9,43	" "
	3	"	"	"	3,93	11,30	" "
Halimba-Cseres							
Sample No.	4	grey	and	pink	bauxite	6,87	18,45
						"	"

The above-compiled average samples show that in these two deposits two thirds to three quarters of the total iron content of grey marcasitic bauxite occurred in the ferrous form.

The formation of grey pyritic-marcasitic bauxite is due to a secondary reducing process. — In primary bauxite, forming the bulk of the deposit,

ferrous oxide content can greatly vary according to analysis results, from a minimum of 0,04 per cent (Gánt—Harasztos) to a maximum of 1,72 per cent (Cseres). However, most of the data were grouped around the averages of Table 12.

According to this table, the greatest average ferrous oxide contents were found in the Halimba-Cseres and Tormáskút localities (0,70 and 0,60 per cent, respectively). Further there is a relatively great value at the Izamajor locality (0,54 per cent). At the rest of the occurrences the average ranges from 0,17 to 0,43 per cent. The smallest average percentage of ferrous oxide occurred at the Tés field (0,11).

The Hungarian average, as computed from the above data, amounts to 0,43 per cent. This value suggests that, except for grey-pyritic-marcasitic bauxite, an insignificant amount of iron in Hungarian bauxites is in the ferrous state.

Finally, it should be pointed out that because of the inordinately small number of ferrous iron determinations, the above-computed averages cannot be considered as anything but tentative information. Most probably these values will be essentially modified by future ferrous oxide determinations to be carried out on a greater scale.

#### *Combined (crystal) water content of bauxite*

Under natural circumstances every bauxite contains more or less chemically unbound water, usually termed moisture. Its quantity is, however, variable, depending on the hydrogeological features of the environment. This is why in our investigations we have only considered the combined water content of bauxite. Its quantity is given by routine analyses under the heading "ignition loss".

The amount of combined water within the bauxite deposit is subjected to less intense variations as was the case with alumina, silica and iron.

Extremals were listed in Table 7. The smallest value was found for the Nagyegyháza field, amounting to 6,0 per cent. However, in most of the localities, minimum combined water content varied from 7 to 11 per cent. On discounting as usually, the lateral one per cent, minimum combined water content was generally raised to 10 to 12 per cent. Consequently, the lower limit of combined water content is rather constant.

The greatest value of combined water percentage hitherto observed in Hungarian bauxite amounted to 38 per cent, found at the Malomvölgy and Sümeg localities. In the remainder it generally ranges from 30 to 36 per cent. There are five occurrences (Zalahaláp, Pilisszántó, Nézsa, Tés and Nagyharsány) where ignition loss does not exceed 21 per cent.

**Table 7**  
*Geochemical parameters of combined water content*

Occurrence	Extremals				Central values			Scatter	
	lower		upper		Arith- metic mean	Median	Mode	Variance	Standard deviation
	100%	99%	99%	100%					
Sümeg .....	8,0	10,0	28,0	38,0	14,3	13,2	12,5		
Nyirád : Darvastó.....	7,0	11,5	26,5	33,0	17,9	17,9	18,5	9,6	± 3,1
„ Deákihegy .....	10,0	10,5	22,5	30,0	13,2	12,6	12,5	5,5	± 2,4
„ Táncsics II. ....	8,0	10,0	25,0	26,0	13,3	12,7	12,5	5,8	± 2,4
„ Izamajor .....	7,0	11,0	20,5	35,0	13,2	12,7	12,5	4,4	± 2,1
Zalahaláp .....	10,0	11,0	17,0	18,0	13,3	13,3	13,5		
Szőc : Vargatanya .....	12,0	12,5	28,0	29,0	18,2	17,7	18,5		
„ Félix II. ....	11,0	12,5	27,5	30,0	17,7	17,3	15,5	10,3	± 3,2
„ Dorottya—Szárhegy	10,0	11,5	27,0	32,0	20,7	20,9	24,5	15,9	± 4,0
„ Nyíreskút .....	10,0	10,5	24,0	26,0	16,2	15,3	12,5		
„ Malomvölgy .....	9,0	11,5	31,0	38,0	18,8	17,0	15,5	19,7	± 4,4
Nagyvázsony .....	10,0	11,0	22,5	23,0	14,4	13,3	12,5		
Halimba : Cseres .....	10,0	10,5	19,5	34,0	13,1	12,6	12,5	4,4	± 2,1
„ Tormáskút .....	7,0	9,5	24,0	37,0	12,8	12,3	12,5	6,2	± 2,5
Városlód : Öreghegy .....	9,0	10,5	21,0	31,0	13,7	13,1	12,5	4,4	± 2,1
Fenyőfő .....	8,0	11,0	20,0	24,0	14,8	14,5	14,5		
Dudar .....	11,0	11,5	27,0	28,0	16,0	14,9	13,5		
Eplény .....	11,0	12,0	21,0	23,0	16,8	17,1	17,5		
Alsópere .....	10,0	10,5	34,0	36,0	14,8	13,4	12,5	21,5	± 4,6
Tés.....	11,0	11,0	18,5	19,0	13,3	13,1	12,5		
Iszkaszentgyörgy :									
Kincses-József ..	10,0	12,5	26,5	35,0	20,0	20,5	21,5	6,8	± 2,6
„ Rákhegy .....	10,0	11,5	25,5	31,0	17,3	17,5	18,5	9,7	± 3,1
Gánt : Bagolyhegy .....	10,0	12,5	21,5	32,0	15,4	15,1	14,5	3,2	± 1,8
Harasztos, Meleges,									
Újfeltárás .....	10,0	12,0	22,0	36,0	14,1	13,8	13,5	2,8	± 1,7
Óbarok—Újbarok—									
Vázsony psz. ....	8,0	10,0	27,0	34,0	16,4	14,5	12,5	22,5	± 4,7
Nagyegyháza .....	6,0	8,0	27,5	29,0	16,0	13,9	12,5	23,0	± 4,8
Pilisszántó .....	7,0	8,0	18,0	20,0	12,2	11,8	11,5		
Nézsza .....	11,0	11,0	18,0	19,0	13,3	13,0	12,5		
Nagyharsány .....	9,0	11,0	18,0	20,0	14,3	14,3	14,5		

These large extremals of combined water content, only occur in insignificant parts of the bauxite body, as they are decreased by as much as 5 to 10 per cent after excluding the lateral one per cent of analyses. Accordingly,



maximum combined water content varies from 20 to 27 per cent in most of the occurrences.

The combined water content of average Hungarian bauxite was computed as to being 15,6 per cent.

On the other hand, the arithmetic mean combined water content of the individual localities is round about 12 to 21 per cent. It reaches its maximum at the Dorottya-Szárhegy and Kincses-József localities (20,7 and 20,0 per cent, respectively).

The median hardly differs from the arithmetic mean — especially in regard to occurrences of small combined water percentage. The difference of the two central values is generally below 1,0 per cent. Of the two, the median is generally smaller; only in some occurrences of large combined water content does it exceed the arithmetic mean (Table 8).

The modes of combined water content are very characteristic. In occurrences below 17 per cent average combined water content, the mode is less than the arithmetic mean, indicating that in these the bulk of bauxite is of relatively small combined water content (11,5 to 13,5 per cent). At the same time, the class interval containing the modal amount of combined water is very much enriched: in some occurrences the modal amplitude is as high as 50 per cent (e.g. Izamajor, Táncsics II, Dült-Nyíres, Harasztos-Újfeltárás), in others it varies from 30 to 40 per cent.

On the other hand, in occurrences of large combined water content the mode increases above the arithmetic mean. In such cases, modal amplitude is much less than in the foregoing ones (10 to 20 per cent).

Frequency percentages were relegated as usual into three groups:

1. Combined water content above 20 per cent;
2. Combined water content 14 to 20 per cent;
3. Combined water content below 14 per cent.

This classification is based on mineralogical considerations to be described more detailedly in the following part of our study to be published later. These investigations have established that, in bauxite samples of combined water content below 14 per cent and of small silica percentage, there is very little hydrargillite (1 to 10 per cent) or none at all, i.e. their main allitic mineral is of monohydratic nature (boehmite or diaspore). If, on the other hand, silica content is large, the dominant mineral will be kaolinite.

In samples containing 14 to 20 per cent of combined water there is a mixed occurrence of mono- and trihydratic minerals. Finally, in samples above 20 per cent the dominant mineral was found to be hydrargillite, monohydrates being absent or only occurring in traces.

Consequently, we may from the above triple classification derive information as to allitic mineral content of the bauxite deposits. As the almost

Table 8

*Comparison of average combined water content with other characteristic parameters*

Occurrence	Arithmetic mean	Difference		Age of immediate cover	Shape of histogram
		to median	to mode		
Dorottya-Szárhegy	20,7	+ 0,2	+ 3,8	1. Eocene	
Kincses-József	20,0	+ 0,5	+ 1,5	1. Eocene	
Malomvölgy	18,8	- 1,8	- 3,3	1. Eocene	
Vargatanya	18,2	- 0,5	+ 0,3	1. Eocene	
Darvastó	17,9	± 0,0	+ 0,6	Pleistocene + 1. Eocene	
Félix II	17,7	- 0,4	- 2,2	1. Eocene	
Rákhegy	17,3	+ 0,2	+ 1,2	1. Eocene	
Eplény	16,8	+ 0,3	+ 0,7	Pleistocene + 1. Eocene	
Óbarok-Ujbarok	16,4	- 1,9	- 3,9	u.Oligocene	
Nyireskút	16,2	- 0,9	- 3,7	1. Pliocene + 1. Eocene	
Nagyegyháza	16,0	- 2,1	- 3,5	u.Oligocene	
Dudar	16,0	- 1,1	- 2,5	1. Eocene	
Bagolyhegy	15,4	- 0,3	- 0,9	1. Eocene	
Fenyőfő	14,8	- 0,3	- 0,3	1. Eocene	
Alsópere	14,8	- 1,4	- 2,3	Aptian	
Nagyvázsony	14,4	- 1,1	- 1,9	Pliocene	
Sümeg	14,3	- 1,1	- 1,8	m.Eocene	
Nagyharsány	14,3	± 0,0	+ 0,2	Aptian	
Harasztos- Ujfeltárás	14,1			1. Eocene	
Városlőd	13,7	- 0,6	- 1,2	1. Eocene	
Zalahaláp	13,3	± 0,0	+ 0,2	Tortonian	
Táncsics II	13,3	- 0,6	- 0,8	Tortonian	
Tés	13,3	- 0,2	- 0,8	Aptian	
Nézsza	13,3	- 0,3	- 0,8	m.Eocene	
Deákihegy	13,2	- 0,6	- 0,7	1. Eocene	
Izamajor	13,2	- 0,5	- 0,7	1. Eocene	
Cseres	13,1	- 0,5	- 0,6	1. Eocene	
Tormáskút	12,8	- 0,5	- 0,3	Turonian	
Pilisszántó	12,2	- 0,4	- 0,7	1. Eocene	

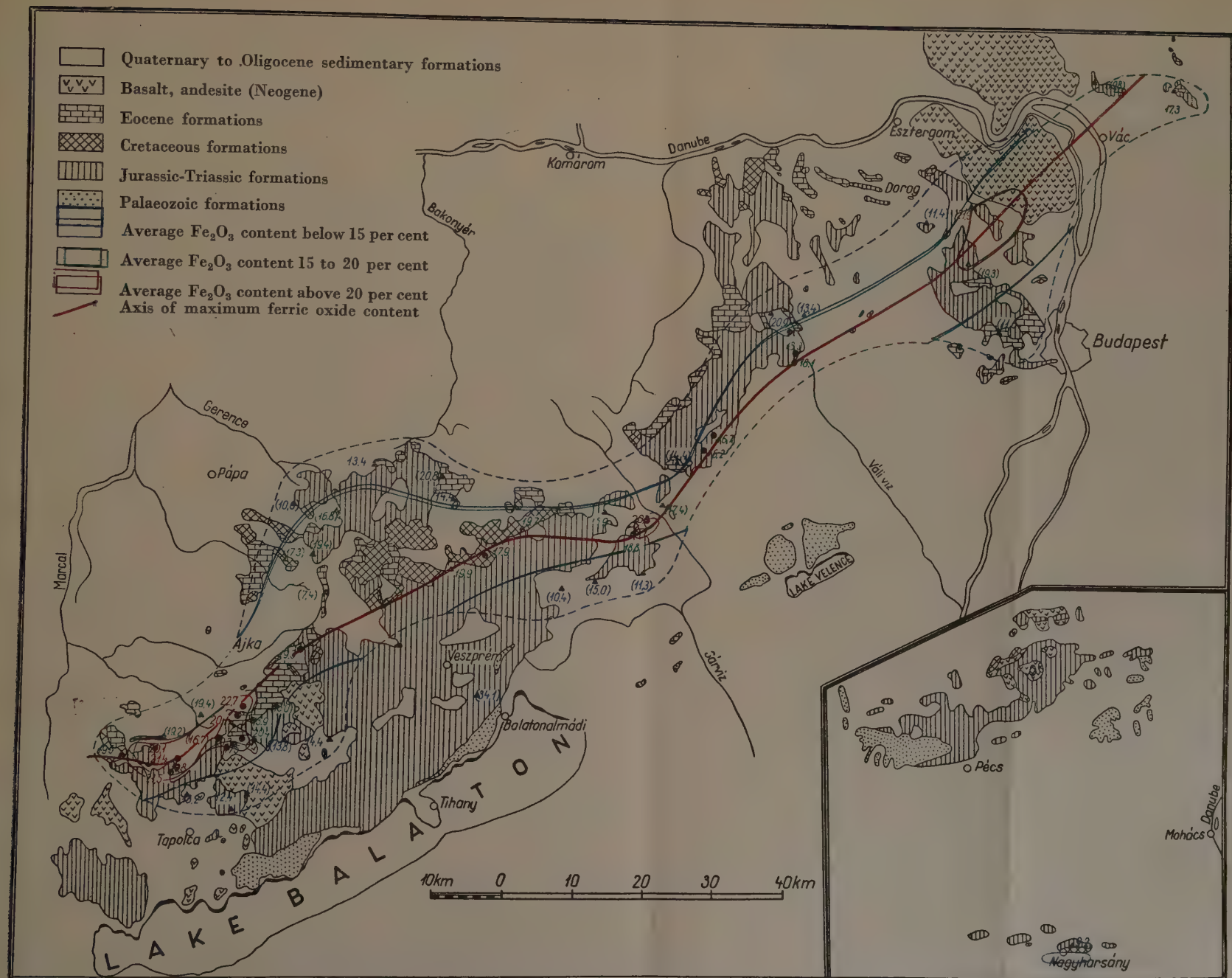


Fig. 8. Average  $\text{Fe}_2\text{O}_3$  content of Hungarian bauxite occurrences

- Larger, thoroughly investigated occurrences
  - ▲ Smaller, less thoroughly known occurrences and superficial indications
- 46,9 Average ferric iron content of occurrence  
(36,0) Uncertain average from small number of data





unique siallitic mineral of bauxite, kaolinite, contains 13,9 per cent of combined water, it also goes in to the first group. However, because of the variance of kaolinite content the above classification can only serve as an approximate orientation.

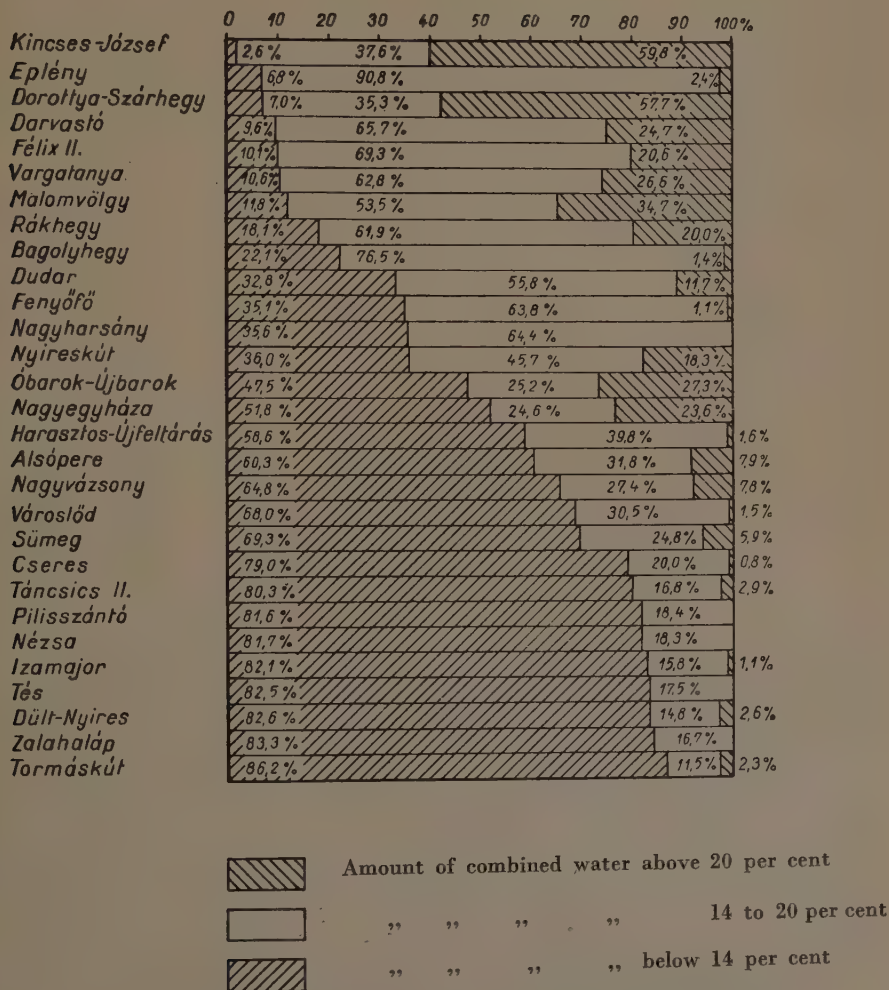


Fig. 9. Frequency distribution of combined water content

32,8: frequency percentages of the three groups

The usual diagrams showing the triple classification were prepared for the individual occurrences and ranged in decreasing order of the group of less than 14 per cent combined water (Fig. 9).

The smallest percentage of bauxite, poor in combined water, was found at the Kincses-József locality (2,6 per cent). In the Szőc, Darvastó, Rákhegy, Bagolyhegy and Nagyharsány deposits it ranges from 7 to 36 per cent. In the remainder of the occurrences, the greater part of the deposit (47 to 86 per cent) is of small combined water content. The largest quantities of bauxite, rich in combined water, occur at the Kincses-József and Dorottya-Szárhegy localities (59,8 and 57,7 per cent, respectively). In eight of the occurrences (Darvastó, Félix II, Nyíreskút, Vargatanya, Malomvölgy, Rákhegy, Óbarok-Újbarok, Nagyegyháza) water-rich bauxite ranges from 18 to 35 per cent. In the remaining 18 it is insignificant (below 10 per cent) or entirely absent.

The section of bauxite with a medium combined water content is rather variable. The Eplény locality shows a maximum percentage of 90,8. There are

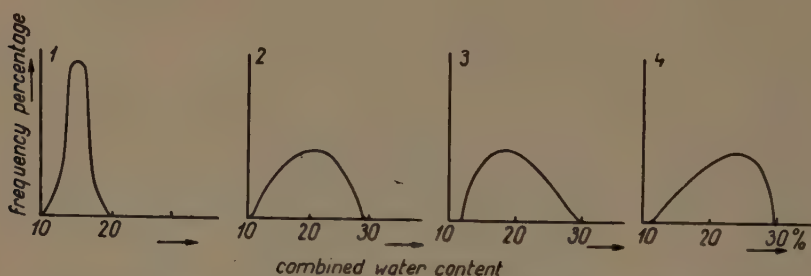


Diagram 4. Typical frequency diagrams of combined water content

other nine occurrences (Darvastó, Vargatanya, Félix II, Malomvölgy, Fenyőfő, Dudar, Bagolyhegy, Nagyharsány, Rákhegy) where it ranges from 55 to 75 per cent: in the remainder its amount is 12 to 40 per cent.

Summarizing the above, we may state that the bulk of bauxite is in most of the occurrences of the low water-content type. The remainder is made up of the medium water-content type, whereas the role played by water-rich bauxite is unimportant. The number of deposits with high combined water percentage is small (two), that of deposits with medium percentage somewhat greater.

Within the histograms of combined water content four groups can be distinguished (Diagram 4).

1. The first group contains the greatest part of the occurrences, 14 in number (Izamajor, Táncsics II, Deákihegy, Cseres, Tormáskút, Harasztos-Újfeltárás, Nagyharsány, Sümeg, Nézsa, Pilisszántó, Tés, Városlőd, Nagy-vázsony, Zalahaláp). The histograms are symmetrical one-peaked ones with an exceedingly sharp peak, modal amplitude being 31 to 49 per cent.

The peak has a somewhat broader flank towards the greater percentages; this, however, causes no skewness, as the amplitudes on this flank are generally



below 1 per cent. The maximum lies in the range of low combined water content (below 14 per cent).

As regards the distribution of combined water, the occurrences of this group are of an entirely homogeneous nature.

2. The histograms of the second group are also symmetrical, but the peak is much broader and, consequently, less high. Modal amplitudes range generally from 13 to 30 per cent. The five pertinent occurrences are Darvastó, Rákhegy, Eplény, Fenyőfő, Bagolyhegy. The peaks occur in the zone of medium combined water content (14,5 to 18,5 per cent).

3. The third group contains 8 localities (Vargatanya, Félix II, Nyíreskút, Alsópere, Dudar, Malomvölgy, Nagygyháza, Újbarok-Óbarok). The peak occurs in the range of medium and/or low combined water content. There is a pronounced skewness on the diagram, the steeper flank being on the side of smaller percentages. Modal amplitude is 12 to 20 per cent, i.e. much less pronounced than in the foregoing groups.

4. In the fourth group there are only two occurrences (Dorottya-Szárhegy and Kincses-József). The histogram of this is approximately the opposite to the foregoing one, with a skewness towards higher combined water percentages. Modal amplitude is 21,5 to 24,5 per cent.

In correlating the above histogram — classification with the average combined water content of the occurrences, the following relationships appear (Table 8):

Deposits of low combined water content are without exception characterized by symmetric and homogeneous histograms. The other three less homogeneous ones appear, on the other hand, with localities of medium to high combined water content. Within this set the largest asymmetry is shown by the two occurrences of the highest combined water content, their skewness pointing towards higher percentages. A similar relation was observed in the case of alumina, silica and ferric oxide. This phenomenon is, however, much more difficult to explain, as it cannot be directly related to the process of bauxitization. In any case, the presence of skewnesses of both kinds points out that there is no monohydratization or trihydratization of a general validity, but that both processes are equally possible. In other words, the process is reversible and its direction is determined by the physico-chemical properties of the environment. Consequently, this process was not impeded by the ending of bauxitization: it still goes on, to this day, although extremely slowly. From the signs of the differences of central values we may, however, conclude that monohydratization is the more general process.

Similarly to the procedure with other components, we have computed the scatter of combined water content data (Table 7). It is found to be smaller than that of the three foregoing components. Average variance is 10,3, the corresponding average standard deviation is 3,2 per cent.

Scatter is the smallest in localities of the smallest combined water content, e.g. the Gánt, Halimba and Nyirád fields, excepting Darvastó.

These is greater scatter at the remainder of the occurrences. This leads to the conclusion that deposits of mainly monohydratic or kaolinitic composition are more homogeneous as combined with water, than those of predominantly trihydratic bauxite. Fig. 10 indicates the relation of combined water content to geographic location and geological position, respectively. It can be seen that there is no such characteristic main strike as was demonstrated for alumina, silica and ferric oxide. On the other hand, the occurrences of the greatest combined water content are seen to occur at the topographically highest sections of the Central Hungarian Mountains.

In the Southwestern Bakony Mountains the localities of high combined water occur throughout at the rim of the Triassic mass, commencing at the Darvastó outcrop and proceeding through the Vargatanya, Félix II and Dorottya occurrences to the Malomvölgy locality. To the North of this chain in the basins of the basement complex, there is a belt of localities poor in combined water. It contains the Tüskésmajor occurrence in the West, the Deákihegy, Táncsics II and Izamajor fields at the center and the Cseres and Tormáskút in the East. Towards the Northeast this belt may be followed through Városlőd to Bakonybél.

At the same time there is a belt of medium combined water content South of the high water-content chain. Chemically it can be said to be of a kaolinitic nature generally. It is made up of the Zalahaláp, Hegyesd, Monostorapáti, Öcs and Nagyvázsony fields.

In the Northern and central parts of the Bakony Mountains, fields of medium to high combined water content occur.

On the Northeastern periphery of the Bakony Mountains, around Iszka-szentgyörgy, combined water content also ranks high. Towards the North and South this region is bordered by small to medium water-content zones. In the Vértes Mountains, bauxite localities are generally of medium combined water content, while in the Pilis Mountains and East of the Danube combined water is medium to low.

Considering the occurrences from the stratigraphical point of view, those with a Cretaceous cover are seen to possess small to medium amounts of combined water (12,8 to 14,8 per cent) (Table 8), whereas those with Eocene cover, small, medium and large percentages are equally possible. The same is the case with fields of Miocene to Pleistocene cover.

There is, on considering the above, no direct relationship between cover age and combined water content, either. It may perhaps be stated, as a first approximation resting on the Cretaceous occurrences that water content decreases with the increase of the cover age.

### *Titanium content of bauxite*

Of the five components determined by routine analyses, the amount of titanium is much smaller than that of the other four. Nevertheless, its quantity is given by each analysis, as titanium is a characteristic component of bauxite, much that it is considered a criterion of a rock being of bauxite. In routine analyses titanium is given in the form of titania, wherefore our investigation will also be based on the percentages of this compound. We have already treated the titanium content of bauxite in an earlier paper [1]. At that time we evaluated 7668 analyses of seven localities. A frequency polygon was constructed for each locality and arithmetic means of titania content were determined. Our present computations have somewhat modified the numerical values of the results, but in their entity this corroborated to the theoretical statements of that paper.

Considering the great homogeneity of titania in bauxite (the order of deviations being some tenths of per cent), we have thought it appropriate to set a class width at one tenth of a per cent instead of the one-per-cent used up till now. This was all the more practical, as the accuracy of routine analyses is just below 0,1 per cent.

The extremes of titania content were listed in Table 9. Minimum titania content hitherto observed in Hungarian bauxite was 0,1 per cent (Darvastó, Alsópere, Pilisszántó). In most of the localities minimum titania content was 0,3 to 0,8 per cent.

After excluding one lateral per cent of analyses, minimum titania content increased to 0,7—1,1 per cent in most of the localities, with the exception of four smaller ones (Alsópere, Zalahaláp, Vargatanya, Pilisszántó) where the extreme was 0,2 to 0,6 per cent.

Maximum titania content showed, on the other hand, a much broader variation. The greatest value so far observed in Hungarian bauxite was 9,9 per cent (Nagygyháza). Maxima ranging from 5 to 7 per cent were demonstrated in the localities Nagyharsány, Óbarok-Újbarok, Izamajor, Darvastó, Dorottya-Szárhegy, Bagolyhegy and Harasztos-Újfeltárás. In the remainder the maximum was found to be 2,5 to 4,5 per cent.

On subtracting the lateral one per cent of analyses, the remarkably great extremes were significantly reduced (by 0,5 to 3,0 per cent). This fact indicates that in most of the occurrences the excessive titania content is restricted to insignificant parts of the deposit. Even after subtraction, the greatest value of 6,1 per cent occurs at the Nagygyháza deposit. This is followed up by the nearby Óbarok-Újbarok locality with 5,5 and by the Dudar one with 4,5 per cent. In the rest of the occurrences the reduced maxima are generally between 2,6 and 4,0 per cent.

Thus the lower limit of titania content is more homogeneous than the



**Table 9**  
*Geochemical parameters of TiO<sub>2</sub> content.*






























Occurrence	Extremals				Central values			Scatter	
	lower		upper		Arith- metic mean	Median	Mode	Vari- ance	Stan- dard deviation
	100%	99%	99%	100%					
Sümeg .....	0,5	0,8	3,0	3,1	1,85	1,86	2,05		
Nyírád : Darvastó .....	0,1	0,5	4,0	5,6	2,18	2,18	2,05	0,35	±0,59
„ Deákihegy .....	0,7	1,0	3,1	4,6	2,15	2,18	2,05	0,26	±0,51
„ Táncsics II. ....	0,4	1,0	3,7	4,1	2,13	2,09	2,05	0,28	±0,53
„ Izamajor .....	0,3	0,8	4,0	6,8	2,17	2,14	2,05	0,37	±0,61
Zalahaláp .....	0,5	0,6	2,1	2,4	1,33	1,44	1,55		
Szőc : Vargatanya .....	0,3	0,4	3,1	3,2	1,41	1,43	1,45		
„ Félix II. ....	0,2	0,8	2,6	3,1	1,64	1,63	1,85	0,15	±0,39
„ Dorottya—Szárhegy	0,6	1,0	2,9	6,1	1,82	1,80	2,05	0,22	±0,47
„ Nyíreskút .....	0,7	1,0	2,9	3,2	1,82	1,83	1,85		
„ Malomvölgy .....	0,4	0,9	3,1	4,0	1,63	1,56	1,55	0,18	±0,42
Nagyvázsony .....	0,6	0,8	2,0	2,1	1,41	1,51	1,55		
Halimba : Cseres .....	0,5	1,2	2,9	3,2	2,02	2,04	2,05	0,15	±0,39
„ Tormáskút .....	0,2	1,0	3,1	3,6	1,95	2,01	2,05	0,18	±0,42
Városlőd : Öreghegy .....	0,2	0,9	2,9	3,6	1,73	1,71	1,25	0,22	±0,47
Fenyőfő .....	0,4	0,7	2,4	2,6	1,40	1,41	1,55		
Dudar .....	1,0	1,0	4,5	4,6	1,79	1,67	1,55		
Eplény .....	0,7	1,5	3,2	3,5	2,41	2,55	2,75		
Alsópere .....	0,1	0,2	3,3	3,6	2,09	2,07	2,05	0,30	±0,55
Tés.....	0,8	0,8	2,6	2,9	1,74	1,76	1,85		
Iszka-szentgyörgy :									
„ Kincses-József	0,9	1,1	3,1	3,6	2,21	2,17	2,05	0,17	±0,41
„ Rákhegy .....	0,5	1,0	2,8	3,0	1,93	1,94	1,95	0,15	±0,39
Gánt : Bagolyhegy .....	0,4	1,0	3,3	5,2	2,17	2,02	2,05	0,23	±0,48
„ Harasztos, Mele- ges, Újfeltárás ....	0,3	1,0	3,1	5,7	2,06	2,07	2,05	0,17	±0,41
Óbarok—Újbarok— Vázsony psz. ....	0,5	1,0	5,5	6,8	2,72	2,64	2,55	0,66	±0,81
Nagyegyháza .....	0,5	1,0	6,1	9,9	2,50	2,50	2,55	0,83	±0,91
Pilis-zántó .....	0,1	0,2	3,1	3,1	2,05	2,00	2,05		
Nézsza .....	1,0	1,1	3,1	3,2	2,17	2,21	2,45		
Nagyharsány .....	0,8	1,1	4,1	6,1	2,90	2,96	3,15		

upper one. Nevertheless, the range of titania percentages is the narrowest of all in the five components.

Arithmetic means, medians and modes of titania distribution are listed in Table 10. Central values were computed to 0,01 per cent precision the

Table 10

*Comparison of average  $TiO_2$  content with other characteristic parameters*

Occurrence	Arithmetic mean	Difference		Age of immediate cover	Shape of histogram
		to median	to mode		
Nagyharsány	2,90	+ 0,06	+ 0,25	Aptian	
Óbarok-Ujbarok	2,72	- 0,08	- 0,17	u.Oligocene	
Nagygyháza	2,50	± 0,00	+ 0,05	u.Oligocene	
Eplény	2,41	+ 0,14	+ 0,34	Pleistocene + l.Eocene	
Kincses József	2,21	- 0,04	- 0,16	l.Eocene	
Darvastó	2,18	± 0,00	- 0,13	Pleistocene + l.Eocene	
Bagolyhegy	2,17	- 0,15	- 0,12	l.Eocene	
Nézsza	2,17	+ 0,04	+ 0,28	m.Eocene	
Izamaajor	2,17	- 0,03	- 0,12	l.Eocene	
Deáki-hegy	2,15	+ 0,03	- 0,10	l.Eocene	
Táncsics II	2,13	- 0,04	- 0,08	Tortonian	
Alsópere	2,09	- 0,02	- 0,04	Aptian	
Harasztos-Ujfeltárás	2,06			l.Eocene	
Pilisszántó	2,05	- 0,05	± 0,00	l.Eocene	
Cseres	2,02	+ 0,02	+ 0,03	l.Eocene	
Tormáskút	1,95	+ 0,06	+ 0,10	Turonian	
Rákhegy	1,93	+ 0,01	+ 0,02	l.Eocene	
Sümeg	1,85	+ 0,01	+ 0,20	m.Eocene	
Nyíreskút	1,82	+ 0,01	+ 0,03	l.Pliocene + l.Eocene	
Dorottya-Szárhegy	1,82	- 0,02	+ 0,23	l.Eocene	
Dudar	1,79	- 0,12	- 0,24	l.Eocene	
Tés	1,74	+ 0,02	+ 0,11	Aptian	
Városlőd	1,73	- 0,02	- 0,48	l.Eocene	
Félix II	1,64	- 0,01	+ 0,21	l.Eocene	
Malomvölgy	1,63	- 0,07	- 0,08	l.Eocene	
Vargatanya	1,41	+ 0,02	+ 0,04	l.Eocene	
Nagyvázsony	1,41	+ 0,10	+ 0,14	Pliocene	
Fenyőfő	1,40	+ 0,01	+ 0,15	l.Eocene	
Zalahaláp	1,33	+ 0,11	+ 0,22	Tortonian	

comparison of deposits possible of sometimes hardly differing averages. The greatest mean of 2,90 per cent is that of the Nagyharsány field. Almost as great (2,72 and 2,50, respectively) are the arithmetic means for the Óbarok-Újbarok and Nagygyháza occurrences. In most (21) of the occurrences the arithmetic mean was found to range from 1,6 to 2,2 per cent.

There were only four occurrences of even smaller means: Vargatanya, Nagyvázsony, Fenyőfő and Zalahaláp, with 1,33 to 1,41 per cent.

The titania content of average Hungarian bauxite was found to be 2,02 per cent. This is in good agreement with the datum (2,00) obtained from the previous paper [1].

The difference of median and arithmetic mean is no more than some hundredths of a per cent. This circumstance points to the remarkably homogeneous and symmetric distribution of titania (Table 10). On the other hand, most of the differences are positive, thus reminding us of the alumina and ferric oxide.

The mode is found with most of the occurrences to lie (16) at 2,05 per cent. This is the most characteristic, the most frequent titania content of our bauxites. The almost complete coincidence of this value with the country average is apparent. This also points to the exceeding homogeneity of titania distribution.

Similarly to the median, the mode is also usually larger than the arithmetic mean. The differences are, however, amounting to some tenths of the per cent.

The frequency percentages of the distribution table were, as usually, condensed in to three groups:

1. Frequency of titania content above 3,0 per cent;
2.     "           "       "       "       "       1,5 to 3,0 per cent;
3.     "           "       "       "       "       below 1,5 per cent.

This classification rests on the observation that a titania content of 1,5 to 3,0 per cent is, according to our experience, characteristic of bauxite. Larger accumulations of titania can be regarded as exceptional, while a titania content below 1,5 per cent, already falls into the average range of argillaceous rocks. Thus, by compiling the analyses of less than 1,5 per cent titania we have determined the amount of bauxites to be considered "argillaceous" from the point of view of titania content.

Figure 11 gives the data in this arrangement of the occurrences. The fact that bauxites of large titania content are subordinate in our bauxites is easily observed. In five occurrences (Rákhegy, Tés, Fenyőfő, Nagyvázsony, Zalahaláp), the titania-rich sort is lacking, while in further the 14 its amount is 0,2 to 2,6 per cent. This group contains, among others, all the fields of the Szőc, Halimba and Gánt environment. Titania-rich bauxite forms 3,6 to 8,1 per



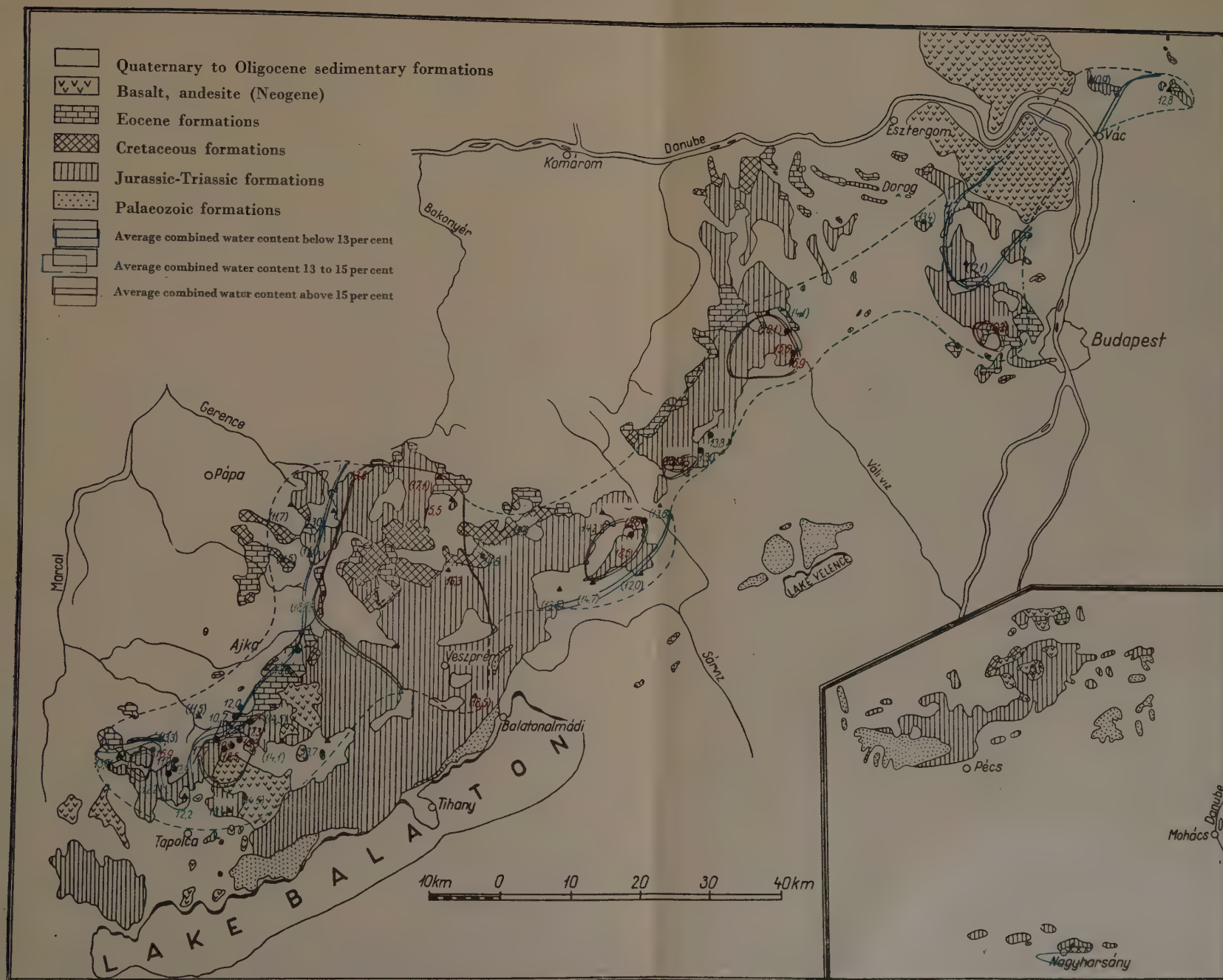
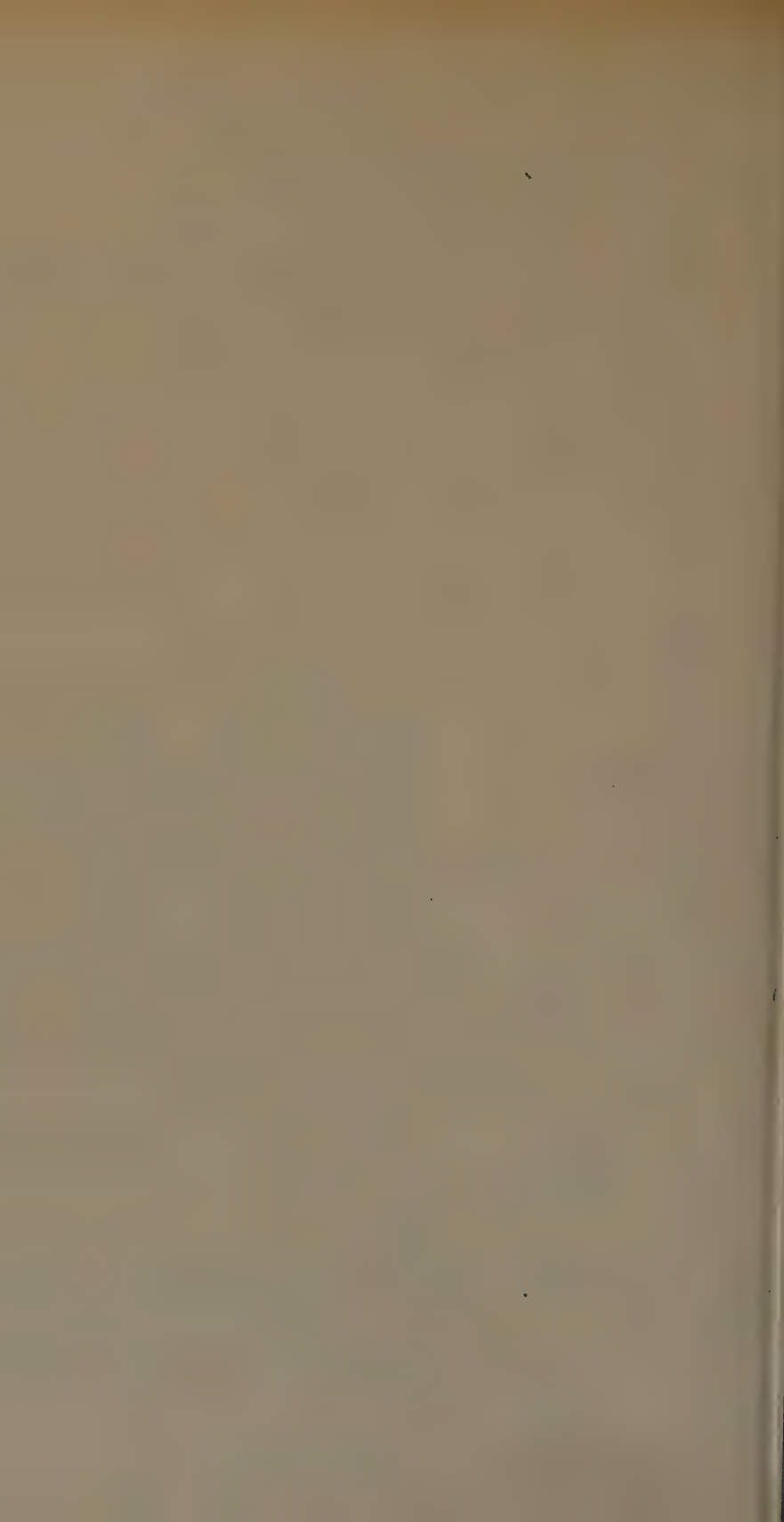


Fig. 10. Average combined water content of Hungarian bauxite occurrences

15,5 Average combined water content of occurrence  
 (11,5) Uncertain average from small number of data

● Larger, thoroughly investigated occurrences  
 ▲ Smaller, less thoroughly known occurrences and superficial indications



**Table II**  
*Main elements of Hungarian bauxite occurrences*

Serial	Occurrence	Average oxydic composition						Elementary composition								Num- ber of Ana- lyses			
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO of this	TiO <sub>2</sub>	Ign. loss	Others	SiO <sub>2</sub> ratio	Free Al <sub>2</sub> O <sub>3</sub> percen- tage	Al	Si	Fe	Ti	O		H	Others from Al	Subtracted from Al <sub>2</sub> O <sub>3</sub> + Ign.
1.	Sümegej	45,9	17,2	19,5	n.m.	1,85	13,6	ca 2,0	2,67	68,2	24,3	8,0	13,6	1,11	51,9	1,52	1,06	1,3 + 0,7	205
2.	Nyírád : Darvástó	47,0	11,5	20,1	0,26	2,18	16,9	2,31	4,08	79,1	24,9	5,4	14,1	1,31	51,2	1,89	1,22	1,27 + 1,04	2009
3.	" Tüskés- major "	47,4	15,5	19,2	0,40	2,24	13,3	2,40	3,06	72,2	25,1	7,2	13,4	1,34	50,2	1,19	1,27	1,65 + 0,75	63
4.	" Deákihegy	50,4	11,0	21,4	0,43	2,15	11,9	3,07	4,58	81,3	26,7	5,1	15,0	1,29	48,9	1,33	1,63	1,80 + 1,27	692
5.	" Tánács II. ....	46,2	17,6	19,8	n.m.	2,13	12,4	1,90	2,63	67,5	24,5	8,2	13,8	1,28	49,8	1,39	1,01	1,02 + 0,88	157
6.	" Izamajor	50,0	11,8	21,5	0,54	2,17	12,2	2,33	4,24	80,0	26,5	5,5	15,0	1,30	49,1	1,37	1,23	1,38 + 0,95	1624
7.	Zalahaláp : Véndekegy	35,7	35,3	13,2	0,31	1,33	12,2	2,29	1,04	16,0	18,9	16,5	9,2	0,80	52,0	1,37	1,21	1,15 + 1,14	168
8.	Nyírád: medence	35,4	28,1	19,4	0,45	1,48	11,5	4,12	1,22	30,1	18,1	13,1	13,6	0,89	50,7	1,42	2,18	1,63 + 2,49	16
9.	Szóc: Vargatanya	40,0	22,8	16,7	0,28	1,41	17,7	1,54	1,76	51,5	21,1	10,7	11,7	0,85	52,9	1,98	0,82	1,03 + 0,51	94
10.	" Félix II. ....	42,1	19,5	17,5	0,17	1,64	16,5	2,82	2,16	60,6	22,3	9,1	12,2	0,98	52,1	1,85	1,49	1,65 + 1,17	552
11.	" Dorottya — Szárhegy "	42,6	13,7	20,3	0,34	1,82	19,9	1,76	3,10	72,5	22,6	6,4	14,2	1,09	52,6	2,23	0,93	0,95 + 0,81	840
12.	" Nyíreskút	43,2	16,9	20,4	0,29	1,82	15,3	2,40	2,55	66,7	22,9	7,9	14,3	1,09	50,8	1,71	1,27	1,46 + 0,94	606
13.	" Malomvölgy	40,0	18,1	19,9	n.m.	1,63	17,8	2,57	2,21	61,5	21,2	8,5	13,9	0,98	52,1	1,99	1,36	1,63 + 0,94	1087
14.	Hegyesd	35,0	36,0	12,4	n.m.	1,16	13,4	ca 2,0	0,97	12,6	18,5	16,8	8,7	0,70	52,7	1,50	1,06	1,3 + 0,7	108
15.	Monostorapáti	34,8	32,8	14,4	n.m.	1,42	14,6	ca 2,0	1,06	19,8	18,4	15,3	10,1	0,85	52,7	1,63	1,06	1,3 + 0,7	60
16.	Örs	35,3	33,4	13,8	n.m.	1,38	14,1	ca 2,0	1,06	19,5	18,7	15,6	9,7	0,83	52,5	1,58	1,06	1,3 + 0,7	62
17.	Nagyvázsöny	34,7	33,8	14,4	n.m.	1,41	13,7	ca 2,0	1,02	17,0	18,4	15,8	10,1	0,85	52,3	1,53	1,06	1,3 + 0,7	230
18.	Halimba: Cseres	45,8	16,3	20,1	0,70	2,02	10,7	5,11	2,81	69,7	24,2	7,6	14,1	1,21	49,0	1,20	2,72	2,70 + 2,13	1148
19.	" Tormáskút	47,7	12,7	22,7	0,71	1,95	12,0	3,02	3,76	77,4	25,3	5,9	15,9	1,17	48,8	1,31	1,60	2,24 + 0,78	2970
20.	Padrag—Kabhegy	34,7	31,1	16,0	n.m.	1,66	14,5	ca 2,0	1,12	23,6	18,4	14,5	11,2	1,00	52,2	1,62	1,06	1,3 + 0,7	41
21.	Városlód: Öreg- hegy	46,0	18,2	19,3	0,37	1,73	13,0	1,82	2,53	66,3	24,4	8,5	13,5	1,04	50,2	1,45	0,95	1,09 + 0,73	1520
22.	Csehbánya	34,9	34,7	7,4	n.m.	1,23	18,8	ca 3,0	1,01	15,5	18,5	16,2	5,2	0,74	56,1	2,22	1,06	1,0 + 2,0	16
23.	Iharkút	45,5	20,1	19,4	n.m.	1,88	11,1	ca 2,0	2,26	62,4	24,1	9,4	13,6	1,13	49,5	1,24	1,06	1,5 + 0,5	5
24.	Bakonnyákó	35,4	32,3	17,3	n.m.	1,46	11,5	ca 2,0	1,10	22,3	18,7	15,1	12,1	0,88	50,9	1,29	1,06	1,5 + 0,5	21
25.	Ugod	37,4	36,9	10,6	n.m.	1,36	11,7	ca 2,0	1,01	16,0	19,8	17,3	7,4	0,82	52,3	1,31	1,06	1,5 + 0,5	12
26.	Bakonymbél	45,9	20,3	16,8	n.m.	1,86	13,0	2,09	2,26	62,3	24,3	9,5	11,7	1,12	50,8	1,45	1,11	1,56 + 0,53	41
27.	Fenyőfő	38,6	30,0	13,4	0,36	1,40	13,8	2,82	1,29	33,9	20,4	14,0	9,1	0,81	52,3	1,51	1,19	1,79 + 1,03	262
28.	Cesznek :																		
29.	Kővölgvárak	13,5	14,4	20,8	0,45	1,90	17,1	2,33	3,02	71,9	23,0	6,7	14,5	1,14	51,5	1,91	1,23	1,29 + 1,01	148
30.	Dudár	38,9	27,8	14,4	0,34	1,79	15,5	1,57	1,40	39,3	20,6	13,0	10,1	1,07	52,7	1,73	0,83	1,12 + 0,45	128
31.	Eplény	45,4	14,0	19,9	n.m.	2,41	16,3	ca 2,0	3,24	73,8	24,0	6,5	13,9	1,44	51,3	1,82	1,06	1,5 + 0,50	252
32.	Alsóperre	45,4	18,3	17,9	n.m.	2,09	14,6	1,71	2,48	65,6	24,0	8,5	12,5	1,25	51,2	1,63	0,91	1,53 + 0,18	171
33.	Tés	38,7	25,0	19,7	0,11	1,74	12,9	2,04	1,55	45,0	20,5	11,7	13,8	1,01	50,4	1,44	1,08	1,61 + 0,43	126
34.	Szentkirály- szabadja	41,1	2,2	34,1	n.m.	2,16	18,5	2,01	18,7	95,4	21,8	1,0	23,8	1,26	49,0	2,07	1,06	1,00 + 1,01	10
35.	Várpalota	34,5	37,4	10,4	n.m.	2,17	13,5	ca 2,0	0,92	7,8	18,3	17,5	7,3	1,30	53,2	1,51	1,06	1,5 + 0,5	3
36.	Inota	33,6	33,5	15,0	n.m.	1,18	14,7	ca 2,0	1,00	15,2	17,8	15,7	10,5	0,71	52,6	1,64	1,06	1,5 + 0,5	7
37.	Csór	32,2	41,5	11,3	n.m.	0,97	12,0	ca 2,0	0,78	0	17,0	19,4	7,9	0,58	52,7	1,34	1,06	1,5 + 0,5	46
38.	Istimér: Vörös- hegy	33,9	32,5	15,9	n.m.	1,50	14,2	ca 2,0	1,04	18,6	17,9	15,2	11,1	0,90	52,3	1,59	1,06	1,5 + 0,5	107
39.	Iszkaszentgyörgy: Kincses-József	49,1	8,2	18,8	0,40	2,21	18,5	3,24	6,00	85,7	26,0	3,8	13,1	1,32	52,0	2,07	1,72	1,78 + 1,16	2510
40.	Iszkaszentgyörgy: Rákhegy	50,8	8,0	20,3	0,35	1,93	15,6	3,41	6,36	86,6	26,9	3,7	14,2	1,16	50,5	1,75	1,81	1,73 + 1,68	1068
41.	Magyaralmás	48,6	16,6	17,4	n.m.	1,84	13,6	ca 2,0	2,93	71,0	25,7	7,8	12,2	1,10	50,6	1,52	1,06	1,5 + 0,5	27
42.	Csákberény	45,9	21,3	14,4	n.m.	1,43	15,0	ca 2,0	2,16	60,6	24,3	10,0	10,1	0,86	52,0	1,68	1,06	1,5 + 0,5	45
43.	Gánt: Bagolyhegy	48,8	16,5	16,2	0,41	2,17	15,0	1,30	2,96	71,3	25,8	7,7	11,3	1,30	51,5	1,68	0,69	0,93 + 0,37	3224
44.	" Harasztos — Melege — Új- feltárás	47,0	18,3	16,7	0,33	2,08	13,8	2,07	2,57	66,8	21,9	8,6	11,7	1,25	50,9	1,51	1,10	1,18 + 0,59	2128
45.	Óbarok — Újbarok — Vázsony psz.	44,2	17,3	18,1	n.m.	2,72	15,9	1,77	2,55	66,7	23,4	8,1	12,7	1,63	51,5	1,78	0,94	1,30 + 0,47	1537
46.	Nagygyeháza	43,0	19,9	18,0	n.m.	2,50	15,6	0,96	2,16	60,7	22,8	9,3	12,6	1,50	51,5	1,75	0,53	0,54 + 0,42	593
47.	Mesterberek	50,0	3,6	20,9	n.m.	3,41	20,1	ca 2,0	13,90	93,8	26,5	1,7	14,6	2,04	51,8	2,25	1,06	1,5 + 0,5	9
48.	Tükrősmajor	48,9	19,2	13,4	n.m.	2,42	14,1	ca 2,0	2,55	66,7	25,9	9,0	9,4	1,45	51,6	1,58	1,06	1,5 + 0,5	5
49.	Budakeszi	33,2	38,2	11,6	0,20	1,66	13,3	ca 2,0	0,87	2,1	17,6	17,9	8,1	1,00	53,1	1,26	1,06	1,5 + 0,5	13
50.	Pilisvörösvár	37,9	26,2	19,3	n.m.	2,51	12,1	ca 2,0	1,45	41,2	20,1	12,2	13,5	1,50	50,3	1,35	1,06	1,5 + 0,5	16
51.	Piliscsaba	35,2	36,0	11,4	n.m.	2,03	13,4	ca 2,0	0,98	13,1	18,6	16,8	8,0	1,22	52,8	1,50	1,06	1,5 + 0,5	7
52.	Pilisszántó	40,6	21,7	21,9	n.m.	2,05	11,7	ca 2,0	1,87	54,4	21,5	10,1	15,3	1,23	49,5	1,31	1,06	1,5 + 0,5	109
53.	Naszál (Szende- hely)	40,5	25,4	19,8	n.m.	1,44	10,9	ca 2,0	1,60	46,7	21,4	11,9	13,8	0,86	49,8	1,22	1,06	1,5 + 0,5	10
54.	Néza	43,2	22,5	17,3	n.m.	2,17	12,8	ca 2,0	1,92	55,8	22,9	10,5	12,1	1,29	50,7	1,43	1,06	1,5 + 0,5	115
55.	Nagyharsány	56,7	15,0	9,2	n.m.	2,90	13,4	2,82	3,78	77,1	30,0	7,0	6,1	1,71	51,9	1,50	1,18	1,15 + 1,37	222

n.m. = not measured





cent of the four Nyirád as well as of the Eplény and Alsópere fields. Finally, there are only four occurrences containing somewhat more important percentages of this type, namely Pilisszentlászló (15,6), Nagyegyháza (22,8), Óbarok-

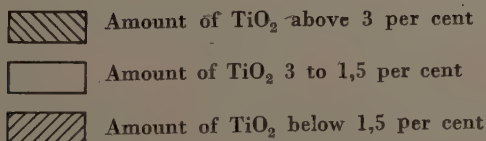
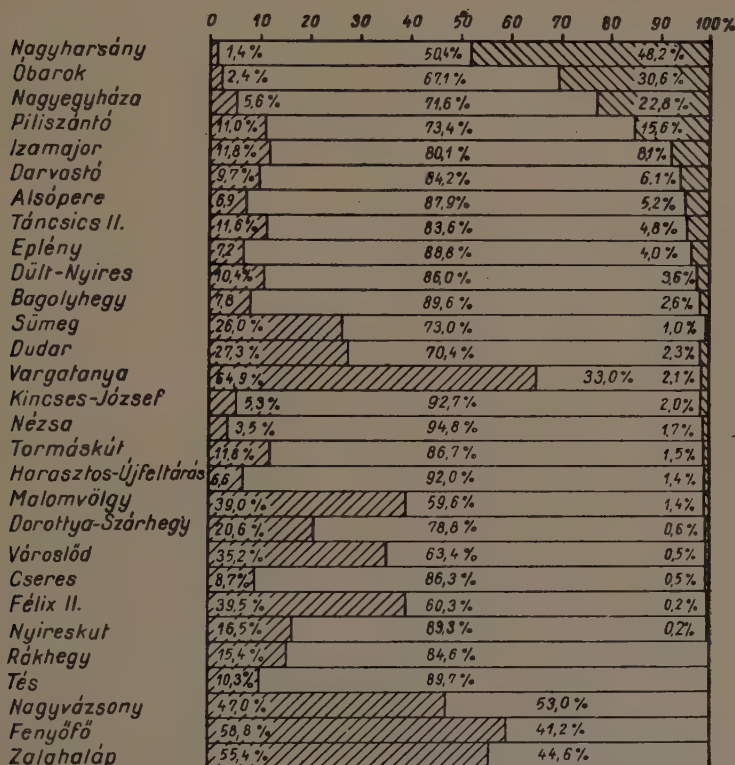


Fig. 11. Frequency distribution of  $\text{TiO}_2$  content

2,6% : frequency percentages of the three groups

Újbarok (30,5) and Nagyharsány (48,2). The last one greatly differs from the occurrences of the Central Hungarian Mountains, as there is a predominance of titania-rich bauxite.

Most of our bauxite deposits in their bulk consist of medium titania content, the accompanying amount of titania-poor bauxite ranging from 3 to

30 per cent. There are no more than four occurrences with more significant masses of this type: Nagyvázsony, Fenyőfő, Zalahaláp and Vargatanya, where 47 to 65 per cent of the deposits consists of titania-poor bauxite. Consequently, as regards the distribution of titania, the bulk of these deposits does not differ from rocks of the clay group. This evidence is corroborated by the fact that the minimum averages of alumina and the maximum ones of silica also occur in these fields.

Because of the exceedingly homogeneous distribution of titania the histograms were likewise constructed with class intervals of one tenth of a per cent. Because of the narrower intervals, there were a number of jutting-

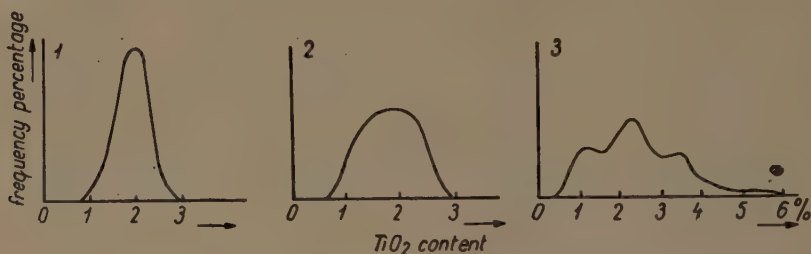


Diagram 5. Typical frequency diagrams of  $\text{TiO}_2$  content

out columns in each histogram. Therefore we have also constructed the histograms of three to five-column running averages. On the basis of these, the groups to be distinguished are as follows (Diagram 5) :

1. The first group contains localities of the most homogeneous distribution, with steep symmetrical peaks. Average titanium content tends to be rather small in this group. (Nagyvázsony, Fenyőfő, Malomvölgy, Vargatanya, Harasztos, Tés, Alsópere, Zalahaláp.)

2. The second group contains the largest number (18) of these localities. The shape of the histograms is variegated, with the common characteristic of a single, rather wide and not too high peak. There are at some points smaller partial maxima superimposed onto the main one. However, these can be ascribed to scatter, and do not suggest a double or triple splitting-up of the modes. In any case, the titania distribution is here less homogeneous than was the case with the first group. The curves are mostly symmetric, with a moderate right-hand skewness at the Nagyarsány, Eplény and Nézsa localities, and an equally moderate left-hand one at the Dudar, Városlőd and Bagolyhegy fields.

3. In the third group there are only three occurrences (Nagyegyháza, Óbarok-Újbarok and Pilisszántó). The curves are the least homogeneous of them all. The wide squat peak is originally composed of 3 to 4 smaller partial maxima. In the Óbarok-Újbarok and Nagyegyháza deposits there is an extended flank towards higher titania percentages.



In Table 10 the shapes of the histograms are compared to average titania content. The first type of histogram is found to be characteristic of localities of small titania content, the third type of those of medium, to a large titania content. Within the most frequent second group the right-hand skewness was coincident with large, the left-hand one with small titania content. As can be observed, the structure of localities of the smallest titania content is the most homogeneous. At occurrences of large titania content, the asymmetry pointing to titanium enrichment is evident in a number of cases. The histograms of the Óbarok-Újbarok and Nagygyháza localities are much different from the rest. As will be seen in a later paper this difference is chiefly due to mineralogical factors.

Scatter of titania content was also computed for localities with a sufficient number of analyses. The mean variance of Hungarian bauxite was found to be 0,29, corresponding to a standard deviation of 0,54 per cent. In most of the occurrences, variance does not differ much from this value. Only with the Nagygyháza and Újbarok-Óbarok localities were much larger values of scatter observed (0,66 and 0,83 of variance and 0,81 and 0,91 of standard deviation, respectively). Consequently, large values of titanium content occur randomly scattered within the bauxite body, and do not form a homogeneous type of enrichment.

The largest homogeneity and the smallest corresponding scatter occurred at the Cseres, Félix II and Rákhegy localities. Dispersion amounted to no more than 0,15, standard deviation to 0,39 per cent (Table 9).

Titania content of the occurrences was also evaluated from the point of view of its geographical and geological position.

The average  $\text{TiO}_2$  content of the localities in the Central Hungarian Mountains exhibits a distribution much resembling that of alumina and ferric oxide. The zone of maximum enrichment strikes parallel to the mountain-chain and fairly coincides with the similar zones for alumina and ferric oxide. The enrichment zone is on both sides bordered by zones of smaller titania content. Within the axis zone the largest enrichment is found to occur in the Northwestern part of the Vértes Mountains (2,5 to 2,7 per cent). Generally speaking, the whole of the Vértes and Pilis Mountains up to Nézsa exhibit intensely enriched titania percentages. Another, rather smaller enrichment, occurs around Eplény and Alsóperre as well as in the Nyirád-Halimba region (Fig 12).

The Nagyharsány locality also stands apart as regards to its titania content, in keeping with its behavior concerning the other components. Its average titania content is the largest of all of them (2,90 per cent). This exceptional enrichment is probably due, besides its different palaeogeographical position also to differences in the mother rock.

Differences in the mother rock also suggest themselves when considering

the above-mentioned high titania concentrations in the Vértes and Pilis Mountains.

There is no correlation of cover rock age to titania content (Table 10). As an illustration one may cite that one of the largest averages is found in a Miocene-covered field, and the smallest one in a Plio-Pleistocene-covered one. Among the Eocene-covered deposits there are also those of very small titania content (Fenyőfő, 1,4 per cent) as well as those of comparatively large ones (Izamajor, 2,2 per cent). Consequently we may state, after having considered all the main components, that the composition of bauxite was controlled by palaeogeographical rather than by stratigraphical-geological factors.

### *Comparison of the quantity of main elements*

Table 11 shows the arithmetic means of all the main components for each of the locality. On the basis of these, the average silica ratio of the individual occurrences was computed as well as the relative percentage of so-called "free" (oxidic and/or hydroxidic) aluminum. Furthermore, the average composition of Hungarian bauxites was, as computed from the averages of the localities, found to be the following :

$\text{Al}_2\text{O}_3$	44,8	per cent
$\text{SiO}_2$	18,0	" "
$\text{Fe}_2\text{O}_3$	18,8	" "
$\text{TiO}_2$	2,0	" "
Ign. loss	15,6	" "
Rest	0,8	" "

Silica ratio 2,9, and 70,3 per cent of the alumina content is present in (oxy)hydroxidic form. According to the classification described in the Introduction, Hungarian bauxite is considered to belong in its entity to "the argillaceous bauxite" type, although within this group it stands rather close to the typical bauxite limit, i.e. 75 per cent of total aluminum in the form of (oxy)-hydrates. This somewhat astonishing result is due to the studies of the entire bauxite deposit instead of only pure bauxite.

The averages of the individual localities differ more or less from the country average. There are fields of expressedly bauxite, argillaceous bauxite, and even of bauxitic clay character.

The spatial distribution of these is shown in Fig. 13. Of course, this arrangement is much resembling the one obtained for alumina frequencies (Fig. 4). Only the fields situated at the archings of the axis line (Halimba, Nyirád and Iszkaszentgyörgy) are of pronounced bauxitic character. Along

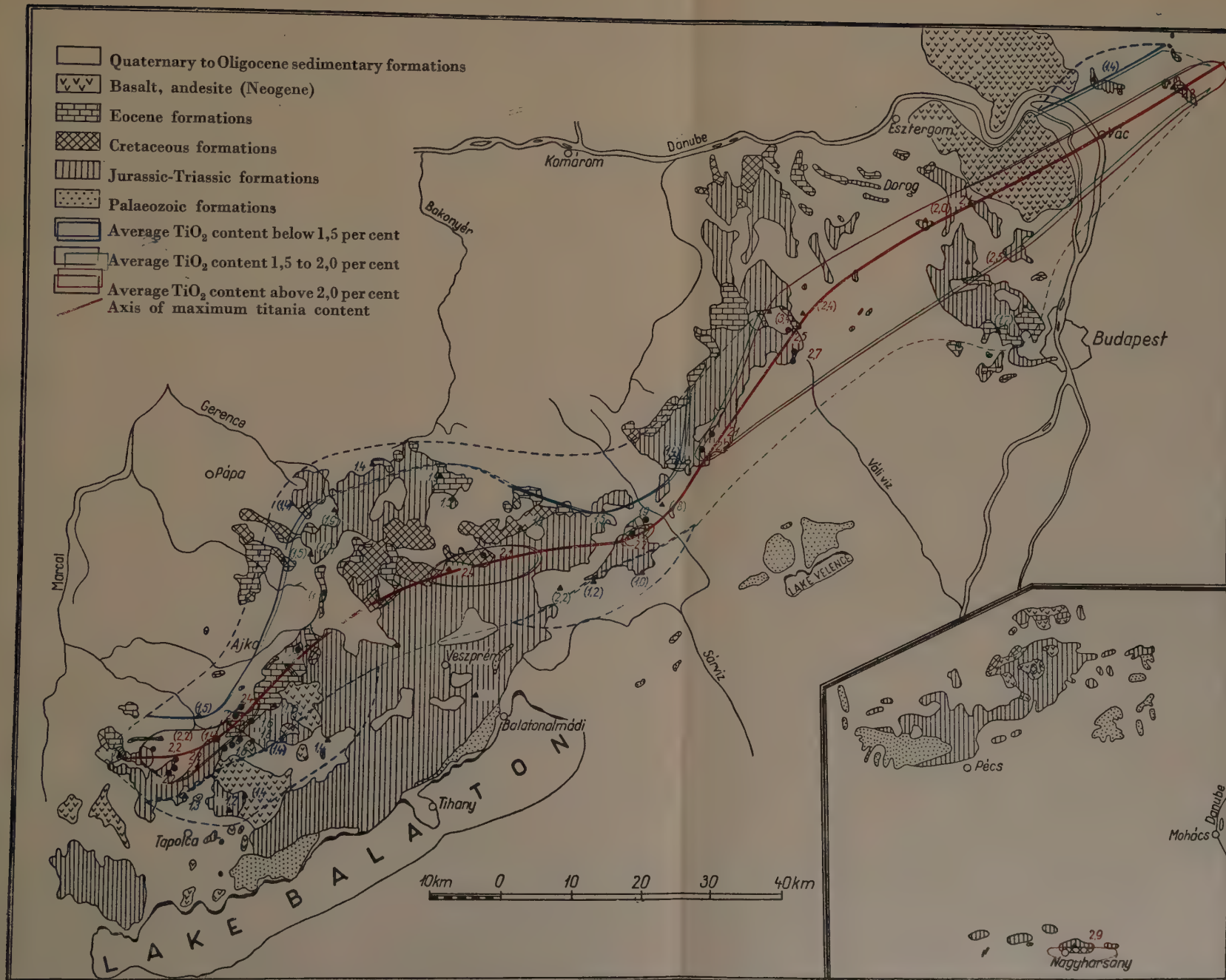


Fig. 12. Average  $\text{TiO}_2$  content of Hungarian bauxite occurrences

- Larger, more thoroughly investigated occurrences
- ▲ Smaller, less thoroughly known occurrences or superficial indications

46,9 Average titania content of occurrences  
(36,0) Uncertain average from small number of analysis





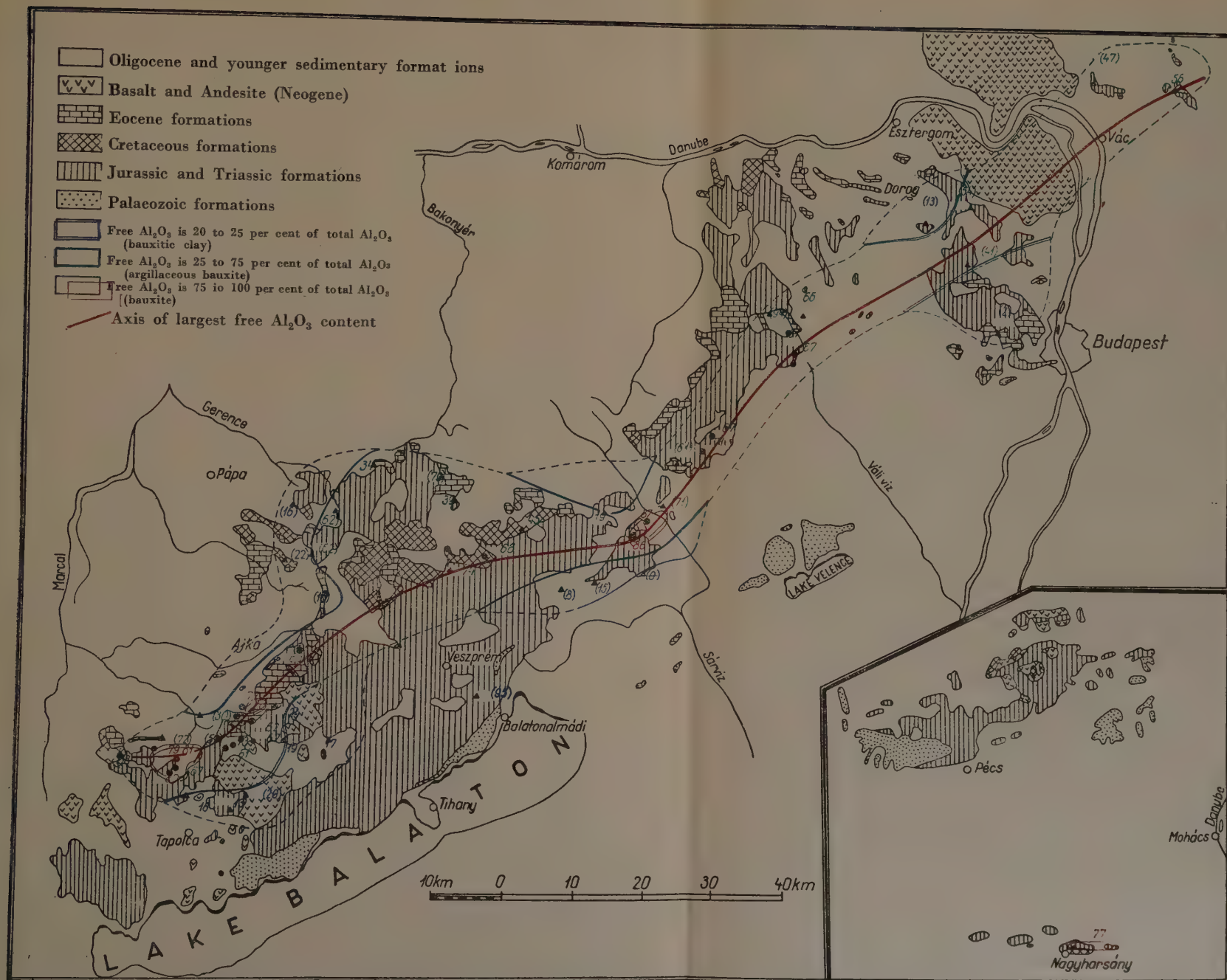


Fig. 13. Relative aluminum hydroxide content of Hungarian bauxite occurrences

- Larger, thoroughly investigated occurrences
- ▲ Smaller, less thoroughly known occurrences and superficial indications

79: Percentage of free (hydroxidic) alumina, related to total alumina, as computed from the average composition of bauxite occurrences





the remainder of the main axis the deposits are of the argillaceous bauxite type, while those on both sides mostly consist of bauxitic clay.

The silica ratio of bauxite deposits varies from 1,05 to 6,6. It is the largest at the Rákhegy locality of Iszkaszentgyörgy and the smallest at the Zalahaláp occurrence.

Using the arithmetic mean composition of the localities, the percentages given in oxydic compounds were recomputed to give elemental composition. The results are also listed in Table 11. Oxygen, averaging 51,3 per cent, is thus demonstrated as being the main element of bauxite. Aluminum follows secondarily, composing exactly one quarter (25 per cent) of bauxite. Iron with 13,1 per cent and silicium with 7,7 per cent follows next. The list is closed with a content of hydrogen and titanium in almost equal quantities (1,74 and 1,21 per cent, respectively). Although the oxygen content of bauxite is mostly left out of the consideration, it is of special interest to us, as the absolute amount of oxygen can be used to express the degree of oxidation of the rock. Now the knowledge of the degree of oxidation is of paramount importance for the geochemical study and for the determination of the genetics of any rock.

Extremal values of the average oxygen content of Hungarian bauxites are 48,8 per cent (Tormáskút) and 52,9 per cent (Vargatanya). As seen, the values do not much differ from the country average, nor do they do so among themselves. These small differences are, nevertheless, very characteristic.

Interesting results are obtained by comparing the above values with the iron oxidation degree of E. SZÁDECZKY-KARDOSS, the so-called " $O_{Fe}$  parameter". This latter is computed, as is known, by the formula

$$O_{Fe} = \frac{2Fe_2O_3}{FeO}.$$

The computation is done by weight percentages [7].

In the course of evaluation we have computed  $O_{Fe}$  values for all the 148 FeO analyses we had to hand. Moreover, the averages of the individual localities were computed, as well as the country average (Table 13). Grey pyritic-marcasitic bauxite was, here also, left out of consideration, for in this type the  $O_{Fe}$  parameter may drop to values of 0,5 to 2,0.

E. SZÁDECZKY-KARDOSS gives 50,1% for the average oxygen content of sediments and 0,33 for the average value of the  $O_{Fe}$  parameter [7, p. 399].

Comparing the average oxygen content (51,3%) and degree of iron-oxidation (102,6) of Hungarian bauxite with the values given by SZÁDECZKY-KARDOSS, the intensely oxidated nature of bauxite can be perceived at once.

There are some interesting relationships to be obtained by comparing the combined water content of bauxite localities with the total oxygen percentage and  $O_{Fe}$  parameter (Table 12). It appears, namely, that the total oxy-

**Table 12**  
*Mineralogical evaluation of combined water content*

Occurrence	Ignition loss	Bound to		Weight percentage of free alumina	Free $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio	Al hydroxide ratios	
		kaolinite	aluminum mineral			Mono-hydrate per cent	Tri-hydrate per cent
Sümeg .....	13,6	5,2	8,4	31,3	3,73	69	31 26
Nyírád : Darvastó.....	16,9	3,4	13,5	37,2	2,76	41	59 54
„ Tüskés major .....	13,3	4,6	8,7	34,2	3,93	73	27 22
„ Deákihegy .....	11,9	3,3	8,6	41,0	4,77	88	12 7
„ Táncsics II. ....	12,4	5,3	7,1	31,2	4,39	82	18 13
„ Izamajor .....	12,2	3,5	8,7	40,0	4,60	85	15 10
Zalahaláp : Véndekhegy .....	12,2	10,6	1,6	5,7	3,56	64	36 31
Nyírád : Basin N. ....	11,5	8,4	3,1	11,5	3,71	68	32 27
Szóc : Vargatanya .....	17,7	6,8	10,9	20,6	1,89	ø	100 95
„ Félix II. ....	16,5	5,8	10,7	25,5	2,38	26	74 69
„ Dorottya—Szárhegy .....	19,9	4,1	15,8	30,9	1,96	4	96 91
„ Nyíreskút .....	15,3	5,1	10,2	28,8	2,82	42	58 53
„ Malomvölgy .....	17,8	5,4	12,4	24,6	1,98	6	94 89
Hegyesd .....	13,4	10,8	2,6	4,4	1,69	ø	100 100
Monostorapáti .....	14,6	9,8	4,8	6,9	1,44	ø	100 100
Öcs .....	14,1	10,0	4,1	6,9	1,68	ø	100 100
Nagyvázsony .....	13,7	10,1	3,6	5,9	1,64	ø	100 100
Halimba : Cseres .....	10,7	4,9	5,8	31,9	5,50	98	2 ø
„ Tormáskút .....	12,0	3,8	8,2	36,9	4,50	84	16 11
Padrag : Kabhegy .....	14,5	9,3	5,2	8,2	1,58	ø	100 100
Városlőd : Öreghegy .....	13,0	5,5	7,5	30,5	4,07	76	24 19
Csehbánya .....	18,8	10,4	8,4	5,4	0,64	ø	100 100
Iharkút .....	11,1	6,0	5,1	28,4	5,57	99	1 ø
Bakonyjákó .....	11,5	9,7	1,8	7,9	4,39	82	18 18
Ugod .....	11,7	11,1	0,6	6,0	10,00	100	ø —
Bakonybél .....	13,0	6,1	6,9	28,6	4,14	77	23 23
Fenyőfő .....	13,8	9,0	4,8	13,1	2,73	40	60 55
Csesznek : Kővölgýárok .....	17,1	4,3	12,8	31,3	2,45	28	72 67
Dudar .....	15,5	8,3	7,2	15,3	2,12	13	87 82
Eplény .....	16,3	4,2	12,1	33,5	2,77	41	59 54
Alsópere .....	14,6	5,5	9,1	29,8	3,27	57	43 38
Tés.....	12,9	7,5	5,4	17,4	3,22	56	44 39
Szentkirályszabadja .....	18,5	0,7	17,8	39,2	2,20	17	83 78
Várpalota .....	13,5	11,2	2,3	2,7	1,17	ø	100 100
Inota .....	14,7	10,0	4,7	5,1	1,09	ø	100 100
Csór .....	12,0	12,4	—0,4	ø	ø?	ø	ø ø

Table 12 continued

Occurrence	Ignition loss	Bound to		Weight percent- age of free alu- mina	Free Al <sub>2</sub> O <sub>3</sub> / H <sub>2</sub> O ratio	Al hydroxide ratios	
		kaolinite	alumi- num mineral			Monohydrate per cent	Trihydrate per cent
Isztimér: Vöröshegy .....	14,2	9,7	4,5	6,4	1,42	ø	100 100
Iszkaszentgyörgy: Kincses-József	18,5	2,5	16,0	42,1	2,63	36	64 59
„ Rákhegy .....	15,6	2,4	13,2	44,0	3,33	59	41 36
Magyaralmás .....	13,6	5,0	8,6	34,5	4,01	75	25 20
Csákberény .....	15,0	6,4	8,6	27,8	3,23	56	44 39
Gánt: Bagolyhegy .....	15,0	4,9	10,1	34,8	3,44	62	38 33
„ Harasztos, Meleges, Újfeltárás .....	13,8	5,5	8,3	31,4	3,78	70	30 25
Óbarok—Újbarok—Vázsony psz.	15,9	5,2	10,7	29,5	2,76	41	59 54
Nagyegyháza .....	15,6	6,0	9,6	26,1	2,72	40	60 55
Mesterberek .....	20,1	1,1	19,0	46,9	2,47	30	70 65
Tükrösmajor .....	14,1	5,8	8,3	32,6	3,93	73	27 22
Budakeszi .....	13,3	11,4	1,9	0,7	0,37	ø	100 100
Pilisvörösvár .....	12,1	7,9	4,2	15,6	3,71	68	32 27
Piliscsaba .....	13,4	10,8	2,6	4,6	1,77	ø	100 100
Pilisszántó .....	11,7	6,5	5,2	22,1	4,25	79	21 16
Naszál .....	10,9	7,6	3,3	18,9	5,73	100	ø ø
Nézsza .....	12,8	6,7	6,1	24,1	3,95	74	26 21
Nagyharsány .....	13,4	4,5	8,9	43,9	4,93	91	9 4

gen and  $O_{Fe}$  parameter tend to have the greatest values with occurrences of large combined water i.e. trihydrate content. (Of course this statement is no more than a tentative one, as the amount of combined water is influenced by the kaolinite content of bauxite as well as by the frequency of alitic minerals.)

To approach this problem with a greater accuracy, the mineralogical composition was computed (Table 12) from the averages of chemical compositions. A basic assumption was that the only form in which silica may be present is kaolinite — an assumption we will prove in the part on bauxite mineralogy to be published in a later paper. The amount of quartz (0,1 per cent) is negligible. Of the total combined water, the amount necessary for the formation of kaolinite was subtracted, and the rest combined to “free” (non-argillaceous) alumina. On the basis of the alumina-to-water ratio thus established, we could assess the amount of “free” alumina in monohydratic and trihydratic bond, respectively. The amount of trihydrates was further diminished by 5 per cent so as to discount the amount of water necessary for goethite. (This procedure will also be justified in the mineralogical part.)

Table 13

*Comparison of degree of oxidation and mineral composition of bauxite*

Occurrence	Computed hydrarg. ratio*	Total O content of bauxite	O <sub>Fe</sub> value**	Combined water per cent***
Budakeszi .....	100	53,1	154,0	13,3
Nagyvázsony .....	100	52,3		13,7
Vargatanya .....	95	52,9	124,4	17,7
Dorottya—Szárhegy .....	91	52,6	130,5	19,9
Malomvölgy .....	89	52,1		17,8
Dudar .....	82	52,7	129,4	15,5
Félix II és I. ....	69	52,1	252,9	16,5
Csesznek .....	67	51,5	112,0	17,1
Kincses-József .....	59	52,0	100,0	18,5
Fenyőfő .....	55	52,3	91,1	13,8
Nagyegyháza .....	55	51,5		15,6
Eplény .....	54	51,3		16,3
Óbarok—Újbarok .....	54	51,5		15,9
Darvastó .....	54	51,2	160,8	16,9
Nyíreskút .....	53	50,8	155,8	15,3
Tés. ....	39	50,4		12,9
Alsópere .....	38	51,2		14,6
Rákhegy .....	36	50,5	107,6	15,6
Bagolyhegy .....	33	51,5	99,9	15,0
Zalahaláp .....	31	52,0	105,8	12,2
Nyírádi medence .....	27	50,7	87,2	11,5
Sümeg .....	26	51,9		13,6
Harasztos—Újfeltárás .....	25	50,9	97,5	13,8
Tüskésmajor .....	22	50,2	(125,4)	13,3
Nézsza .....	21	50,7		12,8
Városlőd .....	19	50,2	108,4	13,0
Piliszántó .....	16	49,5		11,7
Táncsics II. ....	13	49,8		12,4
Tormáskút .....	11	48,8	75,2	12,0
Izamajor .....	10	49,1	88,5	12,2
Deákihegy .....	7	48,9	105,3	11,9
Nagyharsány .....	4	51,9		13,4
Cseres .....	Ø	49,0	74,4	10,7

\* as related to total Al hydroxide content.

\*\* as computed from simultaneous  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  data.

\*\*\* after subtracting accessory elements.



In Table 13 the occurrences were listed in decreasing order of the so composed trihydrate content, and the values of combined water content, total oxygen and  $O_{Fe}$  parameter were compared to it. The latter two were also diagrammatically represented (Fig. 14). In this figure the mentioned covariance of trihydrates with total oxygen and  $O_{Fe}$  parameter becomes apparent. In other words, a greater trihydrate content goes together with a more intense oxydation.

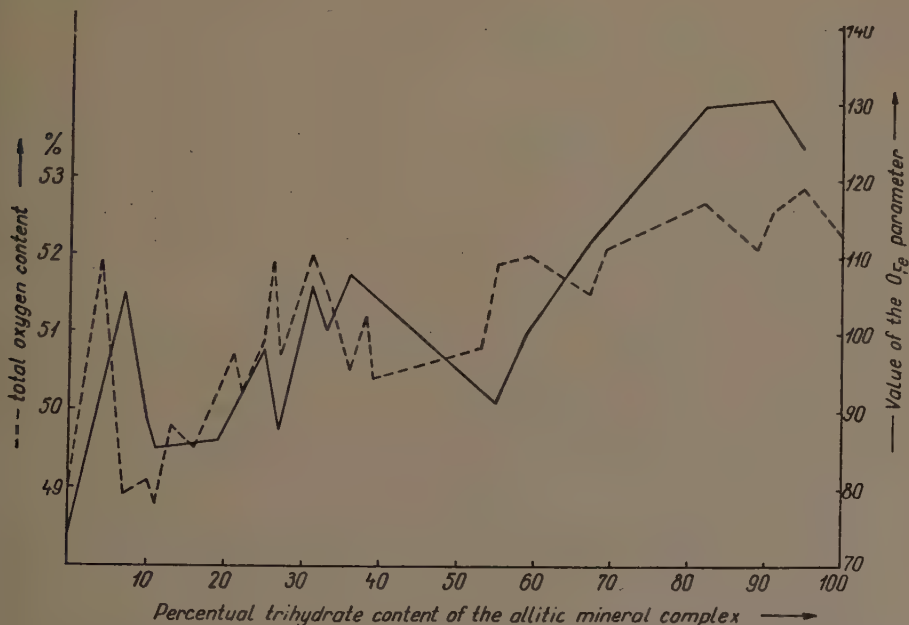


Fig. 14. Relation of degree of oxidation to mineralogical composition in Hungarian bauxite occurrences

The percentual trihydrate content of the allitic mineral complex was also plotted on the geologic map of the Transdanubian Central Hungarian Mountains (Fig. 15). According to this map, the occurrences of great trihydrate content invariably lie topographically at higher parts of the Mountains, while those of smaller trihydrate content are grouped in deeper topographic features around the mass of the mountain.

For this regularity of arrangement we should like to propose the following explanation: The higher-lying occurrences are situated above the main karst water table, whereas the lower ones are inundated by karst water. It is an established fact that the stagnant, badly aerated water masses of karst water shut off the rocks from the possibility of oxidation. At the same time, the rock bodies above the karst water table are in continuous contact with oxygen through the infiltrating superficial waters travelling along joint systems.

As seen above, the trihydratic bauxite occurrences tend to be more intensely oxidated than the monohydratic ones. The approach to this problem from these two angles gives a trivial explanation of the trihydrate-monohydrate problem. Namely, the trihydratic mineralogical composition is due to a greater degree of oxidation, caused by a higher position of karst water above the table.

The above-mentioned are in good agreement with the statements of E. SZÁDECZKY-KARDOSS, according to which bauxite is characterized by very intense oxidation (Geochemistry [6], p. 583).

Of course, the problem is not so simple as all that, because geologic age, thickness of overlying rocks, tectonic activity, etc. can influence the evolution of the mineral character. In this connection we point out the Nézsa, Nagyharsány and Naszál localities where, in spite of topographically high location, bauxite is prevalently monohydratic. However, it was just at these localities that mineralogical analysis demonstrated the presence of diaspore, generally considered to be formed by tectonic processes.

The final conclusion derived from the above, is that the transformation of boehmite into hydrargillite and vice versa is a reversible process mainly controlled by the oxidative potential of the environment. This process goes on to this day, even if very slowly. It will only be ended by the formation of diaspore for some other reasons as this stable modification is unable for further transformation.

We must also give attention to the scatter of the main components, as best characterizing the degree of homogeneity of the rock in question.

The average scatter of the main components of Hungarian bauxite is the following:

	Variance	Standard deviation per cent	Deviation in relative per cents
SiO <sub>2</sub> .....	100,1	10,0	61,0
Al <sub>2</sub> O <sub>3</sub> .....	45,0	6,7	14,2
Fe <sub>2</sub> O <sub>3</sub> .....	28,5	5,3	28,2
Ign. loss .....	10,2	3,2	20,5
TiO <sub>2</sub> .....	0,29	0,54	26,7

It shows that the scatter of the silica content is the largest: bauxite is the least homogeneous in respect to this component. A standard deviation of 10 per cent must be considered as very great indeed.

Alumina and ferric iron content of our bauxite is much more homogeneous and scatter is even smaller with combined water. TiO<sub>2</sub> is a category by itself, being so homogeneous that standard deviation hardly exceeds 0,5 per cent.

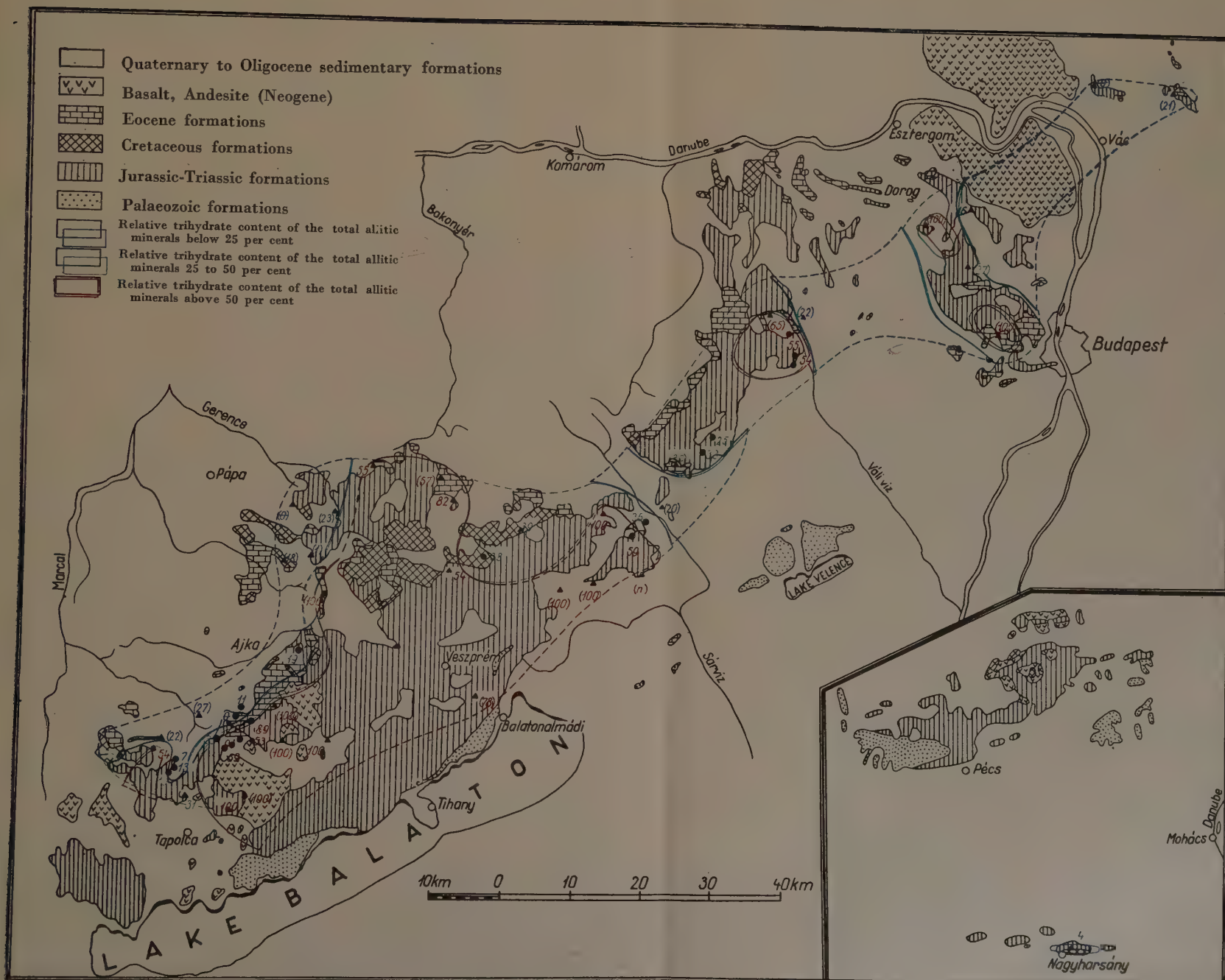


Fig. 15. Ratio of monohydratic to trihydratic bauxite minerals as computed from analyses of Hungarian bauxite occurrences

89 Average relative trihydrate content

(23) Uncertain average from small number of data

● Larger, thoroughly investigated occurrences

▲ Smaller, less thoroughly known occurrences and superficial indications





Standard deviation gives the absolute measure of the deviations from the mean. Geochemically, the computing of the deviations in per cents of the mean is more informative than the variations of the component in question. In this case the standard deviation will be divided by the weighted average of all localities :

$$\mu = \frac{\delta}{m}$$

$m$  being the average weighted by the size of the occurrences,  $\delta$  the standard deviation,  $\mu$  the relative standard deviation. The results are shown in the third column of the above table. The scatter of silica remained the greatest. It is, however, remarkable that alumina should have revealed itself as the most homogeneous (14,2 per cent). This correct inasmuch as an absolute standard deviation of 6,7 per cent is rather small, in proportion to the most frequent component (42,7 per cent). Similarly remarkable is the fact that the relative scatter of titanium should exceed that of alumina and almost reach that of iron. The reason for this is that an absolute standard deviation of 0,54 per cent is great in proportion to a mean of 2,0 per cent.

An especially important role will be ascribed to the analysis of relative deviations in the following part, dealing with accessory and trace elements.

The substance of the Hungarian bauxites in the long run was derived from magmatic rocks. For this reason it is useful to consider the amount of concentration or decentration of the elements of bauxite exhibit with respect to their concentration in magmatic rocks. The data for the average composition of magmatic rocks were taken from the "Geochemistry" of E. SZÁDECZKY-KARDOSS [7, p. 550].

Element	Magmatic average per cent	Hungarian bauxite per cent	Enrichment factor
Al.....	8,13	25,0	+3,08
Si.....	27,72	7,7	—3,60
Fe.....	5,00	13,1	+2,62
Ti.....	0,44	1,21	+2,75

Consequently, of the main elements of bauxite, aluminum is the most enriched; titanium and iron follow next, while the amount of silicium decreases (to about one quarter of the magmatic percentage).

It is essential and by no means incidental that the enrichment of aluminum, titanium and iron is approximately equal, namely about threefold. The enrichment of these components is also geographically coincident (see maps).

The parallel enrichment of these elements in geologically analogous positions show that bauxitization took place under favourable conditions for all of them.

It is known that under magmatic circumstances the three elements do not follow the same course. Iron is siderophile, aluminum lithophile and titanium pegmatophile. Therefore their concentration shows marked differences in the magmatic geophases [7, p. 82]. The covariance of Al and Ti under sedimentary conditions has already been established in our previous paper of 1953 [1]. However, there is no such relation of general validity between Al and Fe and between Fe and Ti, respectively. The remarkable parallel enrichment of these elements in the course of bauxitization may consequently be due to the coincidence of special factors. We intend to deal with these problems in our following study.

### Summary

1. There is a close relationship between the shape of the distribution and the mean percentage of the main elements in Hungarian bauxite. The shape of the frequency histogram is indicative to the main characteristics of bauxitization.

2. There is a further close relationship between the enrichment in the particular occurrences and the geographical location of same: the largest enrichment of aluminum, iron and titanium occur along a line parallel to the strike of the main morphologic feature, the Central Hungarian Mountains, while the same line is also the locus of the greatest decentration of silicium.

3. There is no unequivocal relation between the geologic age of the bauxite deposits and the enrichment of the main elements.

4. According to its average oxygen content (51,3 per cent) and its  $O_{Fe}$  parameter, Hungarian bauxite has revealed itself as an intensely oxidated type of rock.

5. There is a relationship between oxygen content,  $O_{Fe}$  parameter and the quantity of water bound to aluminum hydroxides.

6. The quantity of water bound to aluminum hydroxides is covariant to the topographical height of the locality. High localities of high combined water content are situated above the karst water table, low-lying ones of low combined water content occur below the same.

7. On the basis of Points 5 and 6, the transformation of boehmite into hydrargillite and vice versa seems to be a reversible process, the direction of which is controlled by the oxidative potential of the environment.

8. As related to average magmatic rock, there are almost identical factors of enrichment characterizing Al, Fe and Ti in Hungarian bauxite (about 3,0), while silica exhibits a negative factor of 3,6. The parallel enrichment of aluminum, iron and titanium is due to special circumstances prevailing in the course of bauxitization.

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## GEOCHEMIE DER UNGARISCHEN BAUXITE I.

GY. BÁRDOSSY

*Zusammenfassung*

Die geochemische Analyse der ungarischen Bauxite einleitend untersuchte der Verfasser die Menge und die Verteilung der wichtigsten Elemente des Bauxits (Al, Si, Fe, Ti, O, H). Als Grundlage der Untersuchungen dienten nahezu 28 000 Analysen der angeführten Elemente, die Ergebnisse wurden auf mathematisch-statistischem Wege ausgewertet.

Für jedes der bekannten Bauxitvorkommen Ungarns wurde die durchschnittliche chemische Zusammensetzung bestimmt. Außerdem wurden innerhalb eines jeden Vorkommens für jede Komponente die wichtigsten statistischen Parameter (Mediane, Modus, mittlere quadratische Abweichung) und die Häufigkeitsverteilung bestimmt.

Diese Angaben dienten bei der Nachweisung einiger interessanter geochemischer Zusammenhänge als Grundlage. Die Vergleichung der Häufigkeitsverteilung einzelner Elemente hat bezüglich der Bauxitqualität als Funktion der geographischen Lage einen neuen Zusammenhang geliefert. Schließlich gaben die Mengenverhältnisse der wichtigsten Elemente Anlaß zu theoretischen Erwägungen bezüglich der Verteilung von allitischen Mineralen, sowie zu einem Versuch der Erklärung der möglichen Ursachen dieser Verteilung.

## ГЕОХИМИЯ БОКСИТОВ ВЕНГРИИ. I.

ДЬ. БАРДОШИ

*Резюме*

В качестве первого шага геохимического анализа бокситов Венгрии автором были изучены количество и распределение основных элементов боксита (Al, Si, Fe, Ti, O, H). Исследования были проведены при помощи приблизительно 28 000 анализов для каждого из указанных элементов и оценены способом математической статистики.

В связи с всеми известными месторождениями венгерских бокситов был определен их средний химический состав. Кроме этого для каждой составной части в пределах каждого месторождения отдельно были определены важнейшие статистические параметры (медиана, мода, среднее квадратическое отклонение и т. п.), а также распределение частот.

Эти данные служили основанием для выявления некоторых интересных геохимических соотношений. Путем сравнения распределения частот отдельных элементов было получено новое соотношение относительно качества боксита в функции его географического местоположения. Наконец количественные отношения основных элементов представили возможность для теоретических соображений относительно распределения аллитических минералов и для выяснения возможных причин этого распределения.





# THE CHEMICAL COMPOSITION OF MONTMORILLONITE

By

G. CSAJÁGHY, M. EMSZT and K. SZEPESI

By applying the BUZÁGH—SZEPESI process, from bentonites of various origin and composition pure montmorillonite compounds were prepared. On basis of the interpretation of the data of their analyses the following conclusions can be reached:

1. In the tetrahedral sheet  $\text{Si}^{4+}$  is substituted neither by  $\text{Al}^{3+}$ , nor by OH groups.
2. In the octahedral sheet not 1 atom  $\text{Al}^{3+}$  is substituted by 1 atom  $\text{Mg}^{2+}$ , but 2 atoms  $\text{Al}^{3+}$  are substituted by 3 atoms  $\text{Mg}^{2+}$ , thus the substitution proves to be stoichiometric. It may be supposed that in the lattice there are mixed hydrargillite-brucite layers.
3. The crystal lattice of montmorillonite is compensated, in it there is no charge surplus caused by substitution. Consequently, the cation-exchange capacity cannot be caused by the charge surplus brought about by the fact that in the tetrahedral sheet 1 atom  $\text{Si}^{4+}$  is substituted by 1 atom  $\text{Al}^{3+}$  and in the octahedral sheet 1 atom  $\text{Al}^{3+}$  by 1 atom  $\text{Mg}^{2+}$ .
4. Ca is always in an exchangeable position, thus it does not participate in the building up of the montmorillonite crystal lattice.

The name montmorillonite was proposed in 1847 by DAMOUR and SALVETAT for a clay occurring in Montmorillon (France). In the course of the 110 years which have since then elapsed, a considerable number of eminent research workers have been engaged on the investigation of the chemical composition, crystal structure and physical properties of montmorillonite. The researches were made more difficult by the fact that montmorillonite does not occur in a pure state in nature and that its crystals are exceedingly fine-grained. As the grains of the contaminating minerals are usually of a similar size, their separation or the checking of the purity of the montmorillonite encounters many difficulties. A contaminating mineral contents of 2 to 3%, especially when these minerals are in an amorphous state, cannot be recognized by X-ray analysis, DTA investigation or microscopically, yet the substance in question at the same time may contain several contaminating minerals. On the other hand the results of the investigation of contaminated montmorillonite may give rise to a misinterpretation. Therefore, as it has already been emphasized by McCONNELL [1], EARLY, OSTHAUS and MILNE [2], there is an imperative need to produce compounds of adequate purity.

Irrespective of their amorphous, semi-crystalline or crystalline state, the minerals attaining or coming close to colloidal dimensions are appropriately denominated by SEDLETSKY [3] as colloid-disperse minerals. In consequence of their colloidal nature, these minerals, in many respects, show a similar be-

haviour and on the basis of their colloidal properties can easily be segregated from the non-colloid minerals.

Montmorillonite cannot with any certainty be ranged into any of the crystal classes, and up to the present its crystal structure is not elucidated either. Nevertheless, at present we already know as a certainty that montmorillonite has a specific structure, divergent from that of any other colloid-disperse mineral. This is in evidence in the data furnished by X-ray investigations, thermal analyses and, as we are going to see later on, by chemical analyses, too. It is to be expected that the structural difference in question will manifest itself in one — or possibly several — colloid-chemical properties of the mineral. Thus in principle the possibility exists that on this basis it can be separated from the other colloid-disperse minerals.

Starting from another consideration, but fundamentally the same possibility had been exploited by BUZÁGH and SZEPESI [4] in their procedure worked out for the quantitative determination of the montmorillonite contents of alkaline earth metal bentonites. The substance of their procedure can be outlined as follows: by using electrolytes of such alkaline metals, the anions of which form together with the alkaline earth metal an insoluble precipitate, alkaline earth metal bentonites, resp. montmorillonites, can be transformed into alkaline metal bentonites, that is alkaline metal montmorillonites. To accomplish this transformation,  $\text{Na}_2\text{CO}_3$  and  $\text{NaF}$  proved to be the most suitable compounds. In case the electrolyte used for the transformation is applied in an optimum quantity, a stable suspension is obtained, which does not lose its peptizability even after its desiccation over a water bath. The resulting Na-montmorillonite is hydrophilic to such a degree that even in the presence of dehydrating chemicals, *e.g.* alcohol diluted to a proportion of 1:1, it can be peptized without a residue and cannot be deposited from the suspension obtained even by centrifuging, if the speed of the revolutions is not too high. The same cannot be asserted of the remaining colloid-disperse minerals of bentonites. BUZÁGH and SZEPESI by a considerable number of experiments demonstrated that kaolinite, illite, silica sol, as well as other substances lose their peptizability after such a treatment and their suspension can fully be centrifuged from an alcoholic solution.

By employing the procedure briefly expounded above, we succeeded in preparing pure montmorillonite compounds; the products obtained were subjected to chemical analyses. The conclusions inferred from the data obtained are suitable for the close elucidation of the structure of montmorillonite.

The foundations of the hypothesis most generally adopted at present were laid by HOFMANN, ENDELL and WILM [5] in 1933, and modified by MAEGDEFRAU and HOFMANN [6], MARSHALL [7] and HENDRICKS [8] later on. It is a well-known fact that according to this conception montmorillonite is built up, similarly to pyrophyllite, by units consisting of an Al-octahedral

sheet flanked by two Si-tetrahedral ones. This sandwich-type arrangement [2] can be demonstrated by the crystal chemical formula  $\text{Si}_4\text{O}_{10}(\text{OH})_2\text{Al}_2 \cdot n\text{H}_2\text{O}$ .

Montmorillonite corresponding to the theoretical formula does not occur, however, in nature. According to the data obtained from the numerous chemical analyses published in the classical synthetical study by ROSS and HENDRICKS [9], as well as in the papers of other research workers, montmorillonite always contains a variable quantity of iron, magnesium, calcium, sodium, etc. Beyond doubt, one part of these cations is incorporated in the crystal lattice, whilst another part of them is in an exchangeable position. It is a universally accepted opinion that in the tetrahedral sheet one part of the  $\text{Si}^{4+}$  is replaced by  $\text{Al}^{3+}$  and in the octahedral sheet one part of the  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$ . In regard to the fact that in the tetrahedral sheet all four positive charges of the  $\text{Si}^{4+}$  are bound by one oxygen atom each, it is evident that in case a  $\text{Si}^{4+}$  atom is replaced by an  $\text{Al}^{3+}$  atom, one of the negative charges of the oxygen atoms becomes superfluous. The same occurs in the octahedral sheet, too, when an  $\text{Al}^{3+}$  atom is replaced by a  $\text{Mg}^{2+}$  atom.

This idea was so attractive and was gaining ground in special literature, because it gave an excellent explanation from the practical point of view for one of the most significant properties of montmorillonite, viz. for its exceedingly high cation-exchange capacity. The assumption, according to which montmorillonite is in a position to bind the positively charged ions in consequence of its surplus in a negative charge, arising from the result of its replacement in the lattice, seemed to be obvious.

The cation-exchange capacity resulting from replacement cannot, however, be verified by exact experiments. If the cause of the cation-exchange lay in the charge surplus resulting from replacement, the quantity of cations being in an exchangeable position ought to closely adjust itself to the degree of replacement. However, according to the data published in literature and our own experiences, in reality the matter stands otherwise. On this account JOHNSON [10] refuses to admit the assumption according to which there is a connection between the replacement taking place within the lattice and the cation-exchange capacity, and explains the cause of cation exchange by so-called "broken bonds": on the surface of the faces of montmorillonite crystals the chains Si—O, Al—O and Al—OH are interrupted in the direction of the *a* and *b* axes and the broken bonds which in this way come into being bind the cations, being in an exchangeable position.

The HOFMANN—ENDELL—WILM (*HEW*) structure cannot be reconciled with the thermal behaviour of montmorillonite either. During heating montmorillonite loses its water in three parts, consequently upon its DTA curve there appear three endothermal peaks. The first endothermal peak appears at a relatively low temperature, below 300°C, and is presumably connected with the removal of the water molecules occurring between the indi-



vidual layers. Beside this peak two other endothermal peaks can also be observed, one of them at a temperature between 600—700°C and the other between 800—900°C, they may be derived from the released OH-groups. The original *HEW* structure indicates OH-groups only in the octahedral sheet, and it can hardly be imaginable that in the course of heating they would be released in two sharply separated stages. McCONNELL [1] presumes that the endothermal peak appearing between 800 and 900°C derives from the hydroxyl radicals ranged in the tetrahedral sheet. According to his opinion, in the tetrahedral sheet — as well as in the case of the hydrogarnet — the  $\text{SiO}_4$  tetrahedrons are replaced partly by (OH) tetrahedrons or else the OH ions accompanied by Al replace Si ions.

Between the *HEW* structure and the experimental data there appears an inconsistency not only in the manner of water elimination, but also in respect to the released quantity of water. Leaving the isomorphous substitutions out of consideration, the formula corresponding to the *HEW* structure is as follows:  $\text{Si}_4\text{O}_{10}(\text{OH})_2\text{Al}_2 \cdot n\text{H}_2\text{O}$ , or using the old dualistic notation:  $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O}$ . Consequently, in the crystal lattice of montmorillonite to every  $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  group there would appertain one molecule of structural water. However, according to the numerous analytical data, montmorillonite always contains more water than that.

EDELMAN and FAVEJEE [11] in 1940 presented a proposition, which in their opinion is suitable not only for the explanation of the experimentally revealed water surplus, but from which the characteristic physico-chemical properties of the mineral may virtually be read off. Substantially, they maintain the *HEW* structure and only alter the arrangement of the tetrahedral sheet in such a way that the peak of every second tetrahedron does not point inwards, towards the octahedral sheet, but outwards, in an opposite direction. At the peaks of the tetrahedrons pointing outwards instead of O there is OH. Similarly OH groups occupy those peaks of the Al octahedrons, which are not common with the Si tetrahedrons. To the structure suggested by EDELMAN and FAVEJEE corresponds the formula  $\text{Al}_2[(\text{OH})_4\text{Si}_4\text{O}_8(\text{OH})_2]$ .

According to this conception, the (001) face is covered by a broad network of OH ions bound to Si ions which exert a strong polarizing influence on water and other polar molecules. This gives an explanation for the adsorptive properties of montmorillonite. In the opinion of EDELMAN and FAVEJEE the cation exchange is caused by the fact that the configuration  $\text{Si}(\text{OH})$  is such as that of an insoluble weak acid capable of forming "salts" or in other words capable of exchanging bases for H ions. The defect of this very remarkable hypothesis lies in the fact that it presupposes more OH groups than the cation-exchange capacity of montmorillonite requires. Therefore EDELMAN recently modified the original idea in such a way that only about 20% of the tetrahedrons point outwards. In the opinion of GRIM [12], however, it remains



undecided even in such a case, whether the modified structure will be supported by the data of the X-ray analysis or not.

MARSHALL [7] mentioned as early as 1935, that the arrangement of the Si and Al layers in the montmorillonite on principal allows for two isomers :

Si      Al

Al and Si. In recent times there also exist followers of the second alternative.

Si      Si

In 1955 FRANZEN, MÜLLER-HESSE and SCHWIETE [13] presented a new suggestion regarding the structure of montmorillonite. In their opinion the sheets are not symmetrically arranged in the layer (tetrahedral sheet — octahedral sheet — tetrahedral sheet), but two tetrahedral sheets are united like the  $\alpha$ -quartz and on these lies the octahedral sheet. The formula corresponding to this arrangement is as follows :  $\text{Al}_2[\text{Si}_4\text{O}_9(\text{OH})_4]$ , thus it contains four OH groups in contradiction to the two OH groups of HOFMANN's formula and the six OH groups of the formula proposed by EDELMAN and FAVEJEE.

Regarding the fact that concerning the structure detailed data have not yet been given by them, in the opinion of HOFMANN [14] it can only be ascertained that the behaviour of montmorillonite in the course of cautious desiccation proves to be more favourable to the assumption of two OH groups ; in addition the results of the FOURIER analysis also favour the symmetrical arrangement of the silicate layers.

The analytical data of the original bentonite samples utilized in our experiments are summarized in Table I.

The analytical data refer to air-dry samples. Instead of  $110^\circ\text{C}$  as customary in silicate analyses,  $-\text{H}_2\text{O}$  was determined at  $280$  to  $300^\circ\text{C}$ , because at this temperature in case of the montmorillonite the adsorbed water can be better separated from the water bound in the crystal lattice. It can be seen from the table that the chemical composition of the bentonite samples shows considerable divergences. The sample of Istenmezeje and especially that of Komlóská contain a considerable  $\text{SiO}_2$  surplus.

From the same samples by applying the BUZÁGH—SZEPESI process we have prepared Na-montmorillonites, which with the exception of the sample from Wyoming were converted into H-montmorillonites. As the determination of the  $\text{H}_2\text{O}$ , being in various bonds, encountered analytical difficulties, which were further increased by some organic substances contained in the samples, following the conceptions of MARSHALL [7] the analytical data are indicated as converted into the values for a substance ignited at  $1000^\circ\text{C}$  (Table II).

Leaving the substitutions out of consideration, the formula for ideal montmorillonite can be written in the form  $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$ . In a totally dehydrated state this gives the following general formula :  $\text{Si}_4\text{Al}_2\text{O}_{11}$ . Taking into regard that in connection with ignited samples some of the analytical uncertainties are eliminated, the analytical data of the ignited samples can be

**Table I**  
*Chemical analyses of the original bentonite samples*

	1 %	2 %	3 %	4 %	5 %
SiO <sub>2</sub> .....	77,39	54,96	50,26	61,49	57,23
TiO <sub>2</sub> .....	0,03	0,17	0,35	0,12	0,17
Al <sub>2</sub> O <sub>3</sub> .....	9,35	18,07	17,21	14,15	19,23
Fe <sub>2</sub> O <sub>3</sub> .....	1,01	1,97	2,63	1,62	3,21
FeO .....	0,08	0,19	0,16	0,85	0,36
MgO .....	0,76	2,91	4,71	2,95	2,18
MnO .....	0,01	0,02	0,00	0,00	0,01
CaO .....	0,57	1,63	2,08	1,87	1,27
Na <sub>2</sub> O .....	0,21	0,27	0,14	0,25	2,43
K <sub>2</sub> O .....	0,87	0,51	0,09	0,61	0,39
H <sub>2</sub> O—300 °C .....	7,24	15,34	17,93	11,85	7,86
H <sub>2</sub> O + 300 °C .....	2,36	3,92	4,49	4,05	4,94
P <sub>2</sub> O <sub>5</sub> .....	0,04	0,14	0,18	0,07	0,05
CO <sub>2</sub> .....	0,00	0,00	0,00	0,47	0,20
SO <sub>3</sub> .....	0,00	0,03	0,01	0,00	0,74
S.....	0,00	0,50	0,00	0,20	0,00
—O	99,92%	100,63%	100,24%	100,65%	100,27%
	0,00	0,25	0,00	0,10	0,00
	99,92%	100,38%	100,24%	100,55%	100,27%

1. Komlóska, Mine Gallery Mária, Hungary,
2. Végardó, bore hole No. III, Hungary,
3. Budatétény, mean of the upper level, Hungary
4. Istenmezeje, mean of the upper level, Hungary,
5. National Standard, Wyoming, USA.

better compared in themselves as well as with the above-quoted general formula. The analytical data are indicated in Table II.

On the basis of this data it could also be ascertained that from among the components indicated in Table II only Si, Al, Fe and Mg participate in the structure of the montmorillonite crystal lattice. Among the elements building up the crystal lattice, at the beginning we also indicated Ti, but later on eliminated it, for in case it was one of the constructing elements, it ought to have enriched in the prepared pure montmorillonite sample. The data figuring in Table I and II show just the contrary. Extracting the data of the above-indicated four elements from Table II and expressing them in terms of 100%, the values listed in Table III are obtained.

Table II

*Chemical analyses of the purified samples (montmorillonites)**The numeration of the samples is the same as in Table I*

	1 %	2 %	3 %	4 %	5 %
SiO <sub>2</sub> .....	68,86	68,61	68,08	68,69	65,89
Al <sub>2</sub> O <sub>3</sub> .....	25,56	24,85	23,04	22,66	23,99
Fe <sub>2</sub> O <sub>3</sub> .....	2,13	2,76	3,78	3,26	4,10
MgO .....	2,81	3,40	4,96	4,98	2,66
CaO .....	0,62	0,50	0,08	0,59	0,24
Na <sub>2</sub> O .....	0,39	0,13	0,10	0,19	3,09
K <sub>2</sub> O .....	0,09	0,08	0,01	0,08	0,08
TiO <sub>2</sub> .....	0,13	0,15	0,21	0,06	0,13
	100,59%	100,48%	100,26%	100,51%	100,18%

Table III

*The numeration of the samples is the same as in Tables I and II*

	1 %	2 %	3 %	4 %	5 %
SiO <sub>2</sub> .....	69,30	68,87	68,18	68,97	68,18
Al <sub>2</sub> O <sub>3</sub> .....	25,72	24,94	23,07	22,75	24,82
Fe <sub>2</sub> O <sub>3</sub> .....	2,14	2,77	3,78	3,27	4,24
MgO .....	2,83	3,41	4,97	5,00	2,75
	99,99%	99,99%	100,00%	99,99%	99,99%

Reducing, on basis of Table III, the experimentally detected Fe<sub>2</sub>O<sub>3</sub> and MgO into *equivalent* Al<sub>2</sub>O<sub>3</sub> and adding the values in this way obtained to the experimentally obtained Al<sub>2</sub>O<sub>3</sub> values, and working out the formula Si<sub>4</sub>Al<sub>2</sub>O<sub>11</sub> from the data thus obtained, the following results were obtained :

- |                                   |   |
|-----------------------------------|---|
| 1. Komlóska, Mine Gallery Mária   | Si <sub>4,00</sub> Al <sub>2,00</sub> O <sub>11</sub> |
| 2. Végardó, bore hole No. III     | Si <sub>3,99</sub> Al <sub>2,02</sub> O <sub>11</sub> |
| 3. Budatétény, upper level        | Si <sub>3,97</sub> Al <sub>2,04</sub> O <sub>11</sub> |
| 4. Istenmezeje, upper level       | Si <sub>4,01</sub> Al <sub>1,99</sub> O <sub>11</sub> |
| 5. Nat. Stand., Wyoming, U. S. A. | Si <sub>3,97</sub> Al <sub>2,04</sub> O <sub>11</sub> |

These formulae tally excellently with the theoretical formula Si<sub>4,00</sub>Al<sub>2,00</sub>O<sub>11</sub>. The concordance would be considered as being exceedingly satisfactory when bearing in mind that there were two occasions to commit errors, viz. in the

course of the preparation of the samples and during the chemical analysis itself.

From the above-indicated results of the analyses some interesting conclusions may be derived:

In the tetrahedral sheet  $\text{Si}^{4+}$  cannot be substituted neither by  $\text{Al}^{3+}$ , nor by  $\text{Al} + \text{OH}$ , the Si-tetrahedrons cannot be replaced by OH groups, either. If Si were substituted either by Al, or by OH groups, then in accordance with the degree of substitution the material should contain less Si, consequently the index of Si should also be less than 4,00 in the formula computed from the analytical data.

The experimentally determined  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  was added to the experimentally determined  $\text{Al}^{3+}$  after the latter was converted into *equivalent*  $\text{Al}^{3+}$ . Irrespective of the composition of the material or of the degree of substitution, the Al indices computed from the Al values thus obtained showed an excellent concordance and in case of every sample supplied a value of 2,00. This, however, is only possible in the case if in the octahedral sheet not 1 atom  $\text{Al}^{3+}$  is replaced by 1 atom  $\text{Mg}^{2+}$ , but 2 atoms  $\text{Al}^{3+}$  are substituted by 3 atoms  $\text{Mg}^{2+}$ . In other words the substitution is stoichiometric. If the assumption, according to which the lattice structure of montmorillonite is identical to that of pyrophyllite, proves to be true, then it may be assumed that the hydrargillite layers are mixed with brucite layers. The idea of mixed hydrargillite and brucite layers — as an alternative possibility — was also propounded by MARSHALL [7].

The lattice structure of montmorillonite is compensated, there is no charge surplus in it engendered by substitution. Consequently, the universally accepted supposition, according to which cation exchange is caused by the charge surplus produced by the fact that in the tetrahedral sheet 1 atom  $\text{Si}^{4+}$  is substituted by 1 atom  $\text{Al}^{3+}$  and in the octahedral sheet 1 atom  $\text{Al}^{3+}$  by 1 atom  $\text{Mg}^{2+}$ , must be considered to be incorrect. If the cause of cation exchange lay in the substitution taking place in the lattice, then the cation-exchange capacity would exactly be determined by the degree of the substitution. The cation-exchange capacity of the montmorillonite of Istenmezeje ought to be nearly twice as much as that of the montmorillonite of Komlóská and the eponymous clay mineral, coming from Montmorillon, would show this most characteristic feature of the montmorillonites only in an insignificant degree, as its Mg-contents lies below 0,3% [17]. However, the observations prove this statement to be wrong.

Ca is always in an exchangeable position, thus it does not participate in the structure of the montmorillonite crystal lattice. The data indicated in Table II show that the cation exchange could not be perfectly effected. Every sample contains some Ca, Na and K. K is presumably in a non-exchangeable position and issues from the small quantity of illite left over in the compound.



or from some other contamination. There is no doubt, however, that Na is in an exchangeable position, and can therefore, be considered as a measure of the degree to which we succeeded in substituting cations by hydrogen. If with the exception of the Na-montmorillonite from Wyoming the analytical data are arranged in the order of increasing  $\text{Na}_2\text{O}$  values, we find that the quantity of CaO parallelly increases with that of  $\text{Na}_2\text{O}$ . When the value of either of these reaches its lowest level, then the value of the other is at its minimum, too; on the other hand the maximum  $\text{Na}_2\text{O}$  value goes parallel with the maximum CaO value. In other words where cation exchange turns out better, there we find less Ca and inversely.

In comparing the data figuring in Tables I and II we find that the greatest quantity of CaO (2,08%) was found in the bentonite sample of Budatétény, nevertheless from this sample we obtained montmorillonite containing the least quantity (0,08) of CaO, on the other hand the sample of Komlóska, containing the least quantity (0,57%) of CaO furnished montmorillonite with a maximum CaO content (0,67%).

As a third and favourable proof of the supposition, according to which Ca is always in an exchangeable position, we may mention the experimental fact that from the bentonite of Istenmezeje we also produced a montmorillonite containing not 0,59%, but only 0,18% Ca. After all, the quantity of Ca varied pending on the circumstances of the experiments, which is possible only in case Ca is not built into the crystal lattice. Naturally, one of the prerequisites consists in the fact that the circumstances of the experiments must be such that they do not destroy the crystal lattice.

Against the experimental part of our work an objection can be raised that the chemicals applied in preparing the samples have broken up the crystal lattice and thus the material analysed was not a montmorillonite but some substance of an unknown crystal structure. However, the DTA analyses supplied quite regular montmorillonite curves, at the worst some Ca remained in the montmorillonite and appeared in the first endothermal peak. The rheological properties of the samples (viscosity, thixotropy) have also shown values, that were characteristic of montmorillonite. Besides, it can hardly be imagined that exceedingly different basic matters should bring about disintegration products of such a uniform chemical composition, as supplied by the chemical analyses.

Other research workers were also engaged in purifying montmorillonite. EARLEY, OSTHAUS and MILNE [2] treated bentonites with Na-acetate or NaCl and separated the Na-montmorillonites thus produced by centrifuging them of contaminations. However, the compounds obtained did not prove to be pure enough.

MARGARET D. FOSTER [15] dissolved the free  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  by 0,5 N NaOH. The quantity of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , dissolved at the same time from the

lattice, was determined by calculation, and the analytical results corrected, accordingly. M. D. FOSTER [16] in another of her excellent papers published the results of the analyses of twelve montmorillonite samples, purified in this way [Table 2, p. 997.]. Removing from among the analytical results the Si, Al, Fe and Mg values, they were rereckoned to 100%, then the MgO and Fe<sub>2</sub>O<sub>3</sub> converted into *equivalent* Al<sub>2</sub>O<sub>3</sub> and added to the experimentally obtained Al<sub>2</sub>O<sub>3</sub> values. From the values in this way obtained we have computed the indices of Si and Al and have the following results :

1. Amaragosa Valley, Calif.	Si <sub>4.04</sub> Al <sub>1.94</sub>
2. Greenwood, Maine	Si <sub>3.92</sub> Al <sub>2.11</sub>
3. Fort Steel, Wyo.	Si <sub>4.06</sub> Al <sub>1.92</sub>
4. Belle Fourche, S. D.	Si <sub>3.90</sub> Al <sub>2.14</sub>
5. Upton, Wyo.	Si <sub>3.97</sub> Al <sub>2.04</sub>
6. Tatatila, Mex.	Si <sub>4.07</sub> Al <sub>1.91</sub>
7. Nieder-Bayern	Si <sub>4.01</sub> Al <sub>1.93</sub>
8. Rideout, Utah	Si <sub>4.05</sub> Al <sub>1.94</sub>
9. San Antonio, Tex.	Si <sub>4.03</sub> Al <sub>1.96</sub>
10. Santa Rossa, Mex.	Si <sub>3.94</sub> Al <sub>2.08</sub>
11. Burns, Miss.	Si <sub>4.07</sub> Al <sub>1.91</sub>
12. Aberdeen, Miss.	Si <sub>3.92</sub> Al <sub>2.11</sub>
Mean value : Si <sub>3.998</sub> Al <sub>2.003</sub>	

As can be seen, the values obtained and especially the mean value come close to the theoretical value of Si<sub>4.00</sub>Al<sub>2.00</sub>. In contradiction to FOSTER the objection may be raised that the correction calculation employed by her is only correct if Si or Al are in excess ; if both elements are simultaneously in a free state beside montmorillonite, then the computation cannot furnish accurate values. It is also conceivable that beside montmorillonite free Fe<sub>2</sub>O<sub>3</sub> and some clay mineral contaminations, which are not soluble in NaOH, are also present. This is probably the cause of the more or less considerable divergences between some of the values and the theoretical value.

ROSS and HENDRICKS [9] publish in their monumental study the analyses of 54 samples appertaining to the montmorillonite-beidellite series [Table 1, p. 34]. From the first twelve samples we have computed the Si and Al indices in the above-outlined manner. Some of the samples were identical to the samples used by FOSTER. All samples were in their natural state.

1. Santa Cruz, N. Mex.	Si <sub>4.06</sub> Al <sub>1.91</sub>
2. Cilly, Styria	Si <sub>4.05</sub> Al <sub>1.93</sub>
3. Amaragosa Valley, Calif.	Si <sub>4.04</sub> Al <sub>1.94</sub>
4. Tehachpi, Calif.	Si <sub>4.05</sub> Al <sub>1.94</sub>

5. Dixon, N. Mex.	$\text{Si}_{4.03}\text{Al}_{1.96}$
6. Tatatila, Mex.	$\text{Si}_{3.99}\text{Al}_{2.01}$
7. Maricopa, Calif.	$\text{Si}_{4.00}\text{Al}_{2.00}$
8. Conejos quadrangle, Colo.	$\text{Si}_{4.00}\text{Al}_{2.00}$
9. San Diego County, Calif.	$\text{Si}_{4.04}\text{Al}_{1.95}$
10. Nieder-Bayern, Germany	$\text{Si}_{3.97}\text{Al}_{2.03}$
11. Near Rideout, Utah	$\text{Si}_{3.98}\text{Al}_{2.03}$
12. Ardmore, S. Dak.	$\text{Si}_{3.97}\text{Al}_{2.07}$
Mean value :	$\text{Si}_{4.015}\text{Al}_{1.978}$

As can be seen, the values of non-treated natural samples can come close to the theoretical values and indisputably justify the supposition that in the tetrahedral sheet Si is not substituted by anything, whilst in the octahedral sheet the substitution is stoichiometric.

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## CHEMISCHE ZUSAMMENSETZUNG DES MONTMORILLONITS

G. CSAJÁGHY, M. EMSZT und K. SZEPESI

*Zusammenfassung*

Aus Bentoniten verschiedener Herkunft und Zusammensetzung wurden mit dem Buzágh-Szepesi'schen Verfahren reine Montmorillonitpräparate hergestellt. Bei der Auswertung der bei der Analyse dieser Präparate erzielten Ergebnisse konnten folgende Schlüsse gezogen werden:

1. In der Tetraederschicht wird  $\text{Si}^{4+}$  weder durch  $\text{Al}^{3+}$ , noch durch OH-Gruppen substituiert.
2. In der Oktaederschicht wird nicht ein Atom  $\text{Al}^{3+}$  durch ein Atom  $\text{Mg}^{2+}$ , sondern zwei Atome  $\text{Al}^{3+}$  durch drei Atome  $\text{Mg}^{2+}$  substituiert, die Substitution ist also stöchiometrisch. Es kann angenommen werden, daß das Gitter gemischte Hydrargillit-Brucitschichten enthält.
3. Das Kristallgitter des Montmorillonits ist ausgeglichen, durch Substitution hervorgerufene Überschußladung ist darin nicht vorhanden. Demzufolge kann die Kationaustauschfähigkeit nicht durch jene Überschußladung verursacht werden, die dadurch entsteht, daß in der Tetraederschicht  $\text{Si}^{4+}$  durch  $\text{Al}^{3+}$  und in der Oktaederschicht  $\text{Al}^{3+}$  durch  $\text{Mg}^{2+}$  substituiert wird.
4. Ca ist stets in einer austauschbaren Position, nimmt also am Bau des Montmorillonit-Kristallgitters nicht teil.

## ХИМИЧЕСКИЙ СОСТАВ МОНТМОРИЛЛОНИТА

Г. ЧАЯГИ, М. ЭМСТ и К. СЕПЕШИ

*Резюме*

Применением способа Бузаг—Сепеши из бентонитов различного происхождения и состава были приготовлены чистые монтмориллонитовые соединения. На основании интерпретации полученных при их анализе результатов можно сделать следующие выводы:

1.  $\text{Si}^{4+}$  в тетраэдровом слое не замещается ни  $\text{Al}^{3+}$ , ни OH-группами.
2. В октаэдровом слое не один атом  $\text{Al}^{3+}$  замещен одним атомом  $\text{Mg}^{2+}$ , а два атома  $\text{Al}^{3+}$  замещены тремя атомами  $\text{Mg}^{2+}$ , таким образом замещение является стехиометрическим. Предполагается, что в решетке располагаются смешанные гидраргиллито-бруцитовые слои.
3. Кристаллическая решетка монтмориллонита компенсирована, в ней нет избытка заряжения, вызванного замещением. Следовательно мощность катионного обмена не может представлять собой следствие избытка заряжения, вызванного тем обстоятельством, что в тетраэдровом слое один атом  $\text{Si}^{4+}$  замещен одним атомом  $\text{Al}^{3+}$  и в октаэдровом слое один атом  $\text{Al}^{3+}$  замещен одним атомом  $\text{Mg}^{2+}$ .
4. Са всегда находится в изменяемом положении, таким образом он не участвует в строении кристаллической решетки монтмориллонита.



# ÜBER HYDROPARAGONIT, EIN NEUES GLIMMER-MINERAL, SOWIE ÜBER SEINE BEZIEHUNGEN ZUM HYDROMUSKOVIT, NATRONILLIT UND BRAMMALLIT

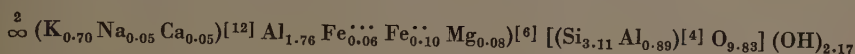
Von

J. ERDÉLYI, V. KOBLENCZ und V. TOLNAY

AUS DER UNGARISCHEN GEOLOGISCHEN ANSTALT

(Eingegangen am 6. Mai 1957.)

1. Das Tonmineral von Nagybörzsöny ist ein, dem Muskovit nahestehender Hydromuskovit, dessen spezielle Konstitutionsformel auf Grund der Analyse I.

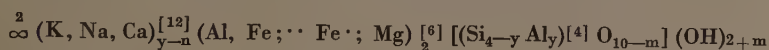


ist.

2. Dieser Hydromuskovit und der von ihm begleitete Erzgang sind mesothermalen Ursprungs. Der Hydromuskovit von Nagybörzsöny steht dem Muskovit näher, als das Vorkommen von Ogofau, welches epithermalen Ursprungs ist [9].

3. Im Hydromuskovit tritt der OH—Überschuß an die Stelle der O-Ionen der Tetraederschicht, und nimmt die Zahl der Alkalimetallionen ab. Die Zahl der O-Ionen der Tetraederschicht nimmt mit soviel ab, als sich die Äquivalentenzahl der HO-Ionen erhöht.

So ist die allgemeine Strukturformel des Hydromuskovits folgende:



Es wäre durch weitere Untersuchungen, und genaue Analysen festzustellen, ob der Zusammenhang  $n = m$  besteht, der bei dem Hydroparagonit von Fenestrella deutlich nachweisbar ist.

4. Auf Grund des Vergleichs unserer Untersuchungsergebnisse, sowie der Untersuchungsdaten anderer Autoren konnte das Bestehen eines neuen Glimmerminerals, des Hydroparagonits zweifellos festgestellt werden.

5. Das unter dem Namen Brammallit beschriebene Mineral ist nicht als Natronillit sondern als Hydroparagonit anzusprechen. Das Bestehen des Natronillits scheint nicht bewiesen zu sein.

Es ist seit langem bekannt, daß durch hydrothermale Vorgänge entstandene Tonminerale oftmals Erzgänge umgeben [1]. Das in den Veränderungshöfen vorkommende, weißfarbige, glimmerartige Mineral beschreiben die Autoren meist als Serizit, ohne daß seine Mineralart genau bestimmt würde. Mit dem Namen Serizit pflegt man in erster Linie den feinkörnigen Muskovit, kann auch den Natronmuskovit und den größten Teil der Hydroglimmer zu bezeichnen, wenn keine näheren Angaben über sie zur Verfügung stehen.

Der Name Serizit ist — nach F. A. BANNISTER [2] — für jeden feinkörnigen Glimmer gebräuchlich, über den keine genauen optischen und röntgenographischen Daten zur Verfügung stehen, und der, auf Grund seiner chemischen Zusammensetzung Paragonit, Muskovit, Hydromuskovit, oder Illit (auch Natronillit — Brammallit) sein kann. Im Besitze genauer Daten ist aber der Name Serizit nicht mehr zulässig. Durch seine Korngröße ist der Hydromusko-

vit vom Illit leicht zu unterscheiden, da der Unterschied zwischen beiden bei ungefähr 50facher Vergrößerung augenscheinlich ist.

Anlaß uns mit der Serizit-Frage zu befassen, gab die Untersuchung des Tonminerals von Nagybörzsöny (Komitat Nógrád in Ungarn).

Die Autoren, die sich mit den Erzgängen von Nagybörzsöny beschäftigen, wie : G. PANTÓ [3, 4] G. KISVARSÁNYI und M. HERRMANN [5], F. PAPP [7], S. KOCH und GY. GRASSELLY [8], betrachten das Tonmineral im allgemeinen als Kaolin, beschäftigen sich aber nicht eingehender mit ihm und ziehen auch keine genetischen Folgerungen aus der »Kaolinisierung«. K. SZTRÓKAY [6] läßt diese Frage in seiner Arbeit unberührt.

Oberflächlich betrachtet erinnert das Tonmineral von Nagybörzsöny an Kaolin, beziehungsweise an Serizit. Bei stärkerer (mindestens 50facher) Vergrößerung ist aber gut ersichtlich, daß es sich um eine aus weißen, oder gelblichen, seidenglänzenden, weichen Glimmerschüppchen mit talkartigem Griff bestehende Masse handelt, deren Eigenschaften mit jenen des aus Ogofau beschriebenen Hydromuskovits nahe übereinstimmen [9]. Im Gegensatz zu dem aus Ogofau stammenden epithermalen Glimmermineral ist aber der Hydromuskovit von Nagybörzsöny vorherrschend mesothermalen Ursprungs, da in Nagybörzsöny die veränderte Zone mächtig und kräftig ist. (Siehe : A. M. BATEMAN [10].) Nach der Ansicht von W. NOLL [11] und R. L. FOLK [12] konnte sich Hydromuskovit nur bei einem Temperaturintervall von 200—525° gebildet haben. Dieses Temperaturintervall wird durch A. M. BATEMANNS Feststellungen verengert [10]. Der aus Ogofau von Carmarthen-shire in England von A. BRAMMALL und Mitarbeitern [9] beschriebene Hydromuskovit ist ohne Zweifel epithermalen Ursprungs, da die veränderte Zone schmal erscheint. (A. M. BATEMAN [10].) Auffallend ist die Ähnlichkeit bei den Vorkommen Nagybörzsöny und Ogofau auch darum, weil die begleitenden Minerale in beiden Fällen goldführender Pyrit und Arsenopyrit sind.

A. BRAMMALL und Mitarbeiter [9] charakterisieren den aus Ogofau in England beschriebenen Hydromuskovit als ein weiches, weißes, glimmerartiges Material. Seine analytisch-chemischen Daten [9] stehen jenen des Hydromuskovits von Nagybörzsöny nahe. Aus der Berechnung der Analyseergebnisse, des spezifischen Gewichts und der Daten der Einheitszelle ist — nach BRAMMALL — nachweisbar, daß die Anzahl der O, OH und F-Radikale in den Muskoviten von der Anzahl der OH-Radikale unabhängig, rund 48 beträgt. Dies ist ein beständiger, für den Muskovit charakteristischer Wert. Ist kein F vorhanden, können sich nur O, und OH gegenseitig wechseln. Daraus folgt — nach BRAMMALL —, daß das Mineral über 105° flüchtiges Wasser weder mechanisch gebunden, noch an der Kristalloberfläche adsorbiert enthält.

Nach BRAMMALL und Mitarbeiter [9] weicht der Hydromuskovit vom idealen Muskovit in folgendem ab :

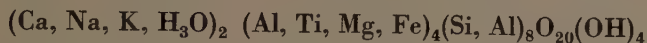
der auf die OH-Gruppen entfallende Anteil ist hoch,  
die Summe der anstatt  $K_4$  sich beteiligenden alkalischen Metalle ist gering,

die anstatt  $Al_8$  auftretende Atomsumme ist niedrig.

Zwecks präziser Definition des Hydroglimmers gab BRAMMALL [9] die Gestaltung der  $(OH)_8K_4Al_8$ -Gruppe, wie folgt an:



A. K. GANGULY [13] (1951), sowie G. BROWN und K. NORRISH [14] (1952) versuchen gleichzeitig, jedoch unabhängig voneinander den hohen Wasser- und niedrigen K-Gehalt mit der Aufnahme von  $H_3O$ -Ionen zu erklären und schreiben für den Hydromuskovit folgende chemische Formel:



Wir erwähnten schon, daß auch die Illite zur Gruppe der Hydromuskovite gehören, aber vom eigentlichen Hydromuskovit beim ersten Betrachten durch ihre Korngröße, die bekanntlich immer innerhalb kolloidaler Grenzen bleibt, abweichen. Chemisch stehen sie dem Pyrophyllit näher als der Hydromuskovit und es ist bekannt, daß es vom letzteren bis zu den echten Glimmern alle Übergänge gibt [15].

Drei Proben des Tonminerals, von drei verschiedenen Stellen des Erbstollens von Nagybörzsöny entnommen, und zwar aus den Gangschnitten No. 1533, 1589 und 1620, wurden durch V. TOLNAY analytisch untersucht. Diese Proben waren mit der Handlupe betrachtet äußerlich verschieden:

*Probe I.*: gelblichweißes, sehr feinkörniges, an Kaolin erinnerndes Material, in welches Kalzitkristalle von mikroskopisch unauspräparierbaren Ausmaßen eingesprengt sind.

Die Schüppchen des Tonminerals haften an den Kalzitkriställchen, dieselben bedeckend. Dieser Befund bezieht sich auch auf die beiden anderen Proben.

Bei der *Probe II* ist die Korngröße viel bedeutender. Schon mit der Handlupe kann man seidenglänzende feinkörnige Glimmerhaufen feststellen, in welche winzige Pyrit- und Arsenopyrit-Kristalle eingebettet sind.

Die *Probe III* ist, mit bloßen Augen betrachtet, ebenfalls eine, aus flockigen, seidenglänzenden Schüppchen bestehende Masse, von vollkommen serizitartigem Äußeren. Bei stärkerer Vergrößerung werden darin zerstreute Kalzit- und Pyritkristalle sichtbar.

Alle drei Proben sind durch ein aus feinen, seidenglänzenden, haarförmigen Kristallfäden bestehendes borhaltiges Mineral — nach A. KOCH's brieflicher Mitteilung (Szeged) Turmalin — verunreinigt.

## Angaben der neuen Analysen

	I. %	II. %	III. %
SiO <sub>2</sub> .....	44,90	42,39	42,12
TiO <sub>2</sub> .....	1,21	1,28	0,84
Al <sub>2</sub> O <sub>3</sub> .....	32,46	30,02	29,27
Fe <sub>2</sub> O <sub>3</sub> .....	1,12	5,52	1,88
FeO .....	1,68	1,06	0,67
MnO .....	0,05	0,04	0,10
CaO .....	2,65	2,42	6,72
MgO .....	0,83	1,10	0,72
K <sub>2</sub> O .....	7,88	7,35	7,15
Na <sub>2</sub> O .....	0,36	0,46	0,22
H <sub>2</sub> O <sup>-</sup> .....	0,52	0,25	0,45
H <sub>2</sub> O <sup>+</sup> .....	4,70	4,88	4,60
CO <sub>2</sub> .....	1,81	0,97	4,56
P <sub>2</sub> O <sub>5</sub> .....	0,22	0,35	0,38
S .....	—	3,89	—
—O .....	—	1,95	—
	100,39	100,12	99,68

Die spektroskopische Untersuchung ergab folgendes Resultat :

keine Probe enthält Co, Ni, Cr. Es waren nachweisbar :

in Probe I Pb : starke Spur, B, Ba, V Spur, Cu und Sn nicht vorhanden:

in Probe II As stark (Zehntel %), B starke Spur, V, Cu, Sn Spur, Pb

schwache Spur, Ba nicht vorhanden :

in Probe III As stark, B, Sn Spur, V, Cu schwache Spur, Pb, Ba nicht vorhanden.

Da ferner jede Probe das Bormineral, Kalzit und Apatit in geringer Menge, Probe II außerdem auch Pyrit und Arsenopyrit, Probe III aber Arsenopyrit enthält, so müssen wir von den Daten der Analyse in Abzug bringen : das P<sub>2</sub>O<sub>5</sub> mit entsprechendem CaO in Form von Apatit, das CO<sub>2</sub> mit der entsprechenden Menge CaO auf Kalzit berechnet, aus Probe II den Schwefel mit einem Teil des Fe<sub>2</sub>O<sub>3</sub> in Form von Pyrit (Bezüglich Probe III siehe weiter unten). Der TiO<sub>2</sub>-Gehalt rührt aller Wahrscheinlichkeit nach auch hier, wie dies beim Hydromuskovit von Ogofau festgestellt wurde [9], von Rutileinschlüssen her und die feinen, den Hydromuskovit stellenweise durchwebenden Kristallfäden sind zum Teil auch als Rutileinschlüsse zu betrachten, so muß auch TiO<sub>2</sub> in Abzug gebracht werden. Endlich wurde aus allen drei Analysen das Adsorptionswasser weggelassen und die so verminderten Prozentsätze dermaßen ergänzt, daß ihre Gesamtsumme wieder die ursprüngliche wurde.



In Probe I entsprechen den 1,82%  $\text{CO}_2$  1,69% CaO und den 0,22%  $\text{P}_2\text{O}_5$  0,29% CaO auf Apatit berechnet. In Probe II entsprechen den 0,97%  $\text{CO}_2$  0,91% CaO und den 0,35%  $\text{P}_2\text{O}_5$  0,46% CaO, insgesamt 1,37% CaO. Den 3,89% Pyritschwefel entsprechen 4,36% FeO und in Betracht genommen, daß der Eisengehalt des Pyrits in der Analyse in Form von  $\text{Fe}_2\text{O}_3$  ausgedrückt wurde, so entsprechen diesem 4,83%  $\text{Fe}_2\text{O}_3$ . Gleichermaßen verfährt man mit dem Karbonat- und Phosphatgehalt der Probe III, wo den 4,56%  $\text{CO}_2$  4,26% CaO und den 0,38%  $\text{P}_2\text{O}_5$  0,50% CaO entsprechen. Insgesamt sind also 4,76% CaO in Abzug zu bringen.

Nach diesen Abzügen und nachdem die Angaben der drei Analysen in der dargelegten Weise umgerechnet wurden, nehmen sie folgende Form an :

	I. %	II. %	III. %
$\text{SiO}_2$ .....	47,62	47,66	47,34
$\text{Al}_2\text{O}_3$ .....	34,43	33,76	32,90
$\text{Fe}_2\text{O}_3$ .....	1,19	0,78	2,11
FeO .....	1,78	1,19	0,75
MnO .....	0,05	0,05	0,11
CaO .....	0,71	1,18	2,20
MgO .....	0,88	1,24	0,81
$\text{K}_2\text{O}$ .....	8,36	8,26	8,04
$\text{Na}_2\text{O}$ .....	0,38	0,52	0,25
$\text{H}_2\text{O}$ .....	4,99	5,48	5,17
	100,39	100,12	99,68

Aus dem Vergleich der drei Analysen ist ersichtlich, daß man es hier, trotz dem verschiedenen Äußeren der drei Proben, mit drei verschiedenen Mustern desselben Minerals zu tun hat. Wegen ihrer Genauigkeit wählten wir Analyse I zum Ausgangspunkt unserer weiteren Berechnungen. Die kristallchemischen Werte berechneten wir aus den Ergebnissen der Proben I und II. Aus Analyse III fehlt der Schwefelgehalt, denn das Prüfungsmaterial erwies sich zur Analyse als ungenügend und konnte nicht ersetzt werden. Deshalb ließen wir Analyse III bei unseren weiteren Berechnungen außer acht.

Die Daten der Analysen I und II in atomarer Zerlegung schreibend, berechneten wir die Ionenzahlen mit Hilfe der Atomquotienten.

Unsere Berechnungen gaben folgende Resultate :

Zum Vergleich geben wir die Ionenzahlen des idealen Muskovits, der mit A und B bezeichneten Hydromuskovite von Ogofau, sowie die, aus den Analyseergebnissen der Proben I und II von Nagyörzsöny berechneten Ionen-

## Analyse I :

	%	Atomquotienten	Ionenzahlen	Ionenzahlen (O+OH=12)
Si .....	22,25	0,7929	792,9	3,12 } 4,00
Al .....	18,23	0,6759	675,9	2,66 { 0,88 } 2,02
Fe :::: .....	0,83	0,0149	14,9	1,78 { 0,06 }
Fe :: .....	1,38	0,0249	24,9	0,10 { 0,08 }
Mg .....	0,53	0,0218	21,8	0,00 { 0,05 }
Mn .....	0,04	0,0007	0,7	0,05 { 0,05 }
Ca .....	0,51	0,0127	12,7	0,70 { 0,83 }
Na .....	0,28	0,0122	12,2	2,17 { 2,17 }
K .....	6,94	0,1775	177,5	9,83 { 9,83 }
OH .....	9,42	0,5539	553,9	3052,6 { 2,17 } 12,00
O .....	39,98	2,4987	2498,7	

## Analyse II :

Si .....	22,26	0,7935	793,5	3,11 } 4,00
Al .....	17,87	0,6626	662,6	2,60 { 0,89 } 1,94
Fe :::: .....	0,55	0,0098	9,8	1,71 { 0,04 }
Fe :: .....	0,93	0,0167	16,7	0,07 { 0,12 }
Mg .....	0,75	0,0308	30,8	0,00 { 0,08 }
Mn .....	0,03	0,0006	0,6	0,06 { 0,06 }
Ca .....	0,84	0,0210	21,0	0,69 { 0,69 }
Na .....	0,39	0,0168	16,8	2,38 { 2,38 }
K .....	6,86	0,1754	175,4	9,62 { 9,62 }
OH .....	10,35	0,6092	609,2	3064,8 { 2,38 } 12,00
O .....	39,29	2,4556	2455,6	

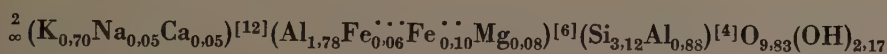
zahlen auf die Einheitszelle berechnet an. Auf Grund obiger Daten kann man auch die spezielle Konstitutionsformel des Hydromuskovits ermitteln.

Der Hydromuskovit von Ogofau ist eine talkähnliche, oder wachsartige Substanz, mit welcher — aller Wahrscheinlichkeit nach — auch andere Tonminerale vermischt sind. Deshalb ist die Summe der Ionenzahlen der Oktaederschicht an sich, samt dem Ca bedeutend geringer als 2 (bezw. 8), während die Summe der Ionenzahlen der Oktaederschicht beim Tonmineral von Nagyborzsöny, innerhalb der Versuchsfehlergrenzen, denen des idealen Muskovits entspricht (2, bezw. 8).

Aus den Angaben ergibt sich, daß der Hydromuskovit von Nagyborzsöny wegen seines 3 : 1 übertreffenden Si : Al Verhältnisses in tetraedrischer Koordination, sowie seines, das Al vertretende Fe- und ziemlich hohen Mg-Gehaltes

Idealer Muskovit		Hydromuskovite:			
		Ogofau A	Ogofau B	Nagybörzsöny I	Nagybörzsöny II
Si	Tetraederschicht {	12	12,48	12,48	12,44
Al		4	3,52	3,52	3,56
Al	Oktaederschicht {	8	7,06	7,12	6,84
Fe <sup>+++</sup>		—	0,14	0,24	0,16
Fe <sup>++</sup>		—	0,08	0,08	0,28
Mg		—	0,20	0,32	0,48
Mn		—	—	—	—
Ca		—	0,04	0,20	0,32
Na	Zwischenschicht {	—	0,10	0,20	0,24
K		4	2,58	2,80	2,76
OH	8	10,86	10,44	8,68	9,52
F	—	0,02	0,04	—	—
O	40	37,12	37,52	39,32	38,48

in oktaedrischer Koordination, und schließlich wegen seines Na-Gehaltes an Stelle des K -s, schon eher in die Gruppe der unter dem Namen Phengite bekannten Muskovitvarietäten einzureihen ist. Auf Grund des obigen kann seine spezielle Konstitutionsformel folgendermaßen veranschaulicht werden :



Mit Berücksichtigung des bisher Gesagten kann man die allgemeine Strukturformel des Hydromuskovits, wie folgt, aufschreiben :



Es ist natürlich, daß wenn  $y = 1$  und  $n = m = 0$  ist, man die Strukturformel des Muskovits erhält.

Teils in Übereinstimmung, teils im Gegensatz zu den obenerwähnten Definitionen, muß man die gegebene Formel als allgemeine Konstitutionsformel des Hydromuskovits annehmen. Es ist nämlich unzweifelhaft, daß die Summe der O- und OH-Ionen in der Strukturformel der Muskovite immer 12 beträgt. Die Bildung der Oxoniumgruppen begründen obenerwähnte Autoren (13,14) in chemischer Beziehung nicht genügend. Dieser spezielle Fall der Oxoniumgruppen, den man richtiger Hydronium, oder Hydroxonium-Ion nennen kann :  $H_3O^+$  ist nichts anderes, als hydratisiertes Hydrogenion, das praktisch nur in den wässrigen Lösungen der Säuren vorhanden ist, aber röntgenographisch auch im festen Hydrat der Perchlorsäure nachgewiesen wurde. Nach der heutigen Auffassung besteht das H-Ion, das Proton

in wässriger Lösung allein nicht, nur in Form seines Hydrats, des Hydroxonium-Ions. Demnach kann die Dissoziation des Wassers, wenn man das H-Ion in wässriger Lösung als Hydrat betrachtet, durch folgende Gleichung ausgedrückt werden :



Diese Gleichung ist aber, wie es im vorigen erwähnt wurde, nur in einer sauren, oder höchstens neutralen Lösung gültig, in einer alkalischen Lösung verschiebt sich das Gleichgewicht nach links. In Betracht gezogen, daß die hydrothermalen Lösungen bei der Bildung des Serizits alkalisch sind, so kann eine dermaßen gedeutete Hydratbildung praktisch nicht zustandekommen, das feste Salz dieses Hydrats, außer dem erwähnten Perchlorat, ist nicht bekannt. Folglich könnte die Hydroxoniumgruppe nicht in das Gitter des in alkalischer Lösung sich gebildeten Hydromuskovits gelangen.

In tetraedrischer Koordination ist die Summe der Si- und Al-Ionen immer 4. Faßt man die Ionenzahlen des Hydromuskovits von Nagyborzsöny ins Auge, so ist es ferner klar, daß in ihm das Si durch 0,88 Al ersetzt ist, dagegen findet man anstatt des diesem entsprechenden 0,88 Äquivalentes K(Na, Ca) nur 0,85 Äquivalente K(Na, Ca).

R. ROY und E. F. OSBORN nehmen im Laufe ihrer mit dem System  $\text{Al}_2\text{O}_3\text{—SiO}_2\text{—H}_2\text{O}$  ausgeführten synthetischen Untersuchungen [16] zur Erklärung der Struktur des von ihnen Hydralsit genannten Silikat-Präparates an, daß wenn in dem  $\text{SiO}_4$ -Tetraeder an Stelle der Si-Ions ein Al-Ion tritt, so wird der Ladungsausgleich dadurch eintreffen, daß an Stelle der O-Ionen OH-Ionen treten. Desgleichen muß man auch die Kristallstruktur des Hydromuskovits auffassen, das heißt, wenn in dem Silikat-Gerüst des Hydromuskovits ein Teil der Si-Ionen durch Al ersetzt wird, so tritt der Ladungsausgleich dadurch ein, daß an Stelle eines Teils der O-Ionen im Silikatgerüst HO-Ionen treten. Parallel mit der Abnahme der negativen Ladungen nimmt somit auch die Zahl der Alkaliionen ab. Die Zahl der HO-Ionen ist aber noch immer höher, als die verminderte Zahl der Alkaliionen. Dies äußert sich in der Abnahme der elektrostatischen Verbindungskräfte der Tetraederschicht und das hat die Abnahme der Kohäsionskräfte des Minerals, d. h. die Zunahme seiner mechanischen Deformierbarkeit zur Folge. Somit nimmt die Härte des Hydromuskovits gegenüber jener des Muskovits ab, und ersterer erhält einen weichen, talkartigen Griff.

Wie beim Hydromuskovit, muß man auch bei dem Illit und Montmorillonit annehmen, daß sie in ihrem Gitter außer den zwei oktaedrisch koordinierten OH-Ionen dieselben auch in der Tetraederschicht enthalten. Diese Voraussetzung ist bei dem Montmorillonit nicht neu. In Bezug auf die Struktur des Montmorillonits wurde sie zuerst von C. H. EDELMANN und



J. C. L. FAVEJEE [17] ausgesprochen. Man findet sie auch mit ausführlicher Erörterung bei D. MCCONNELL [18]. Obige Autoren gründen ihre Auffassung auf die beiden Hochtemperatur-Endothermpunkte der Differential-Thermoanalyse des Montmorillonits. Nach den erwähnten Autoren, wie auch nach R. E. GRIM und W. F. BRADLEY [19], entweicht das Wasser zuerst am niedrigeren Endothermpunkt aus der Oktaederschicht, durch Rehydratation ist aber der ursprüngliche Zustand teilweise noch wiederherstellbar. Am zweiten Hochtemperatur-Endothermpunkt entfernt sich das Wasser aus der Tetraederschicht und der gleich danach folgende Exothermpunkt deutet die tiefgreifende Umänderung der Struktur an.

Die zwei Endothermpunkte der Entweichung des Koordinationswassers beweisen bei den erwähnten Mineralen, daß das Gitter OH-Ionen in Bindungen von zweierlei Energie (in oktaedrischer und tetraedrischer Koordination) enthält. Es ist verständlich, daß bei dem Hydromuskovit durch die Substitution der zwei negativen Ladungen vertretenden O-Ionen mit OH-Ionen, auch die Zahl der Alkalien abnimmt.

Die röntgenographische Untersuchung des Tonminerals von Nagyörzsöny wurde im Röntgenlaboratorium der Ungarischen Geologischen Anstalt durchgeführt. Das DEBYE—SCHERRER'sche Röntgendiagramm des Minerals und die Bemessung der Linien haben K. NAGY und M. MELLES ausgeführt. Röntgenbilder wurden von den Proben I und II aufgenommen. Die beiden Röntgenbilder sind vollkommen identisch. Die Aufnahmen wurden mit  $\text{CuK}\alpha$ -Strahlung und Ni-Filtration ausgeführt. Die Wellenlänge der  $\text{CuK}\alpha$ -Linie wurde aus K. LONSDALE's Angaben errechnet.\* ( $\bar{a} = \frac{2\alpha_1 + \alpha_2}{3} = 1,54145$ ). Die Intensität der Streifen ist mit dem Auge geschätzt worden.

### Bezeichnungen :

Intensität : s.st = sehr stark, st = stark, m = mittel, sch = schwach, s.sch = sehr schwach, d = diffus.

$2\vartheta$  = Glanzwinkel in Graden,

$d_{hkl}$  = Netzebenenabstand in Å.

Aus den Werten der Röntgenaufnahme wurden die Gitterkonstanten des Hydromuskovits berechnet und zum Vergleich in einer Tabelle mit den entsprechenden Angaben des idealen Muskovits [20], des Hydromuskovits von Ogofau [9], des Illits [2], des Kaolinit, des Montmorillonits und des Pyrophyllits [20] zusammengefaßt. Die Gitterkonstanten wurden aus den Angaben der mit 006, 060 und 400 indizierten Netzebenen berechnet.

\* S.: Acta Cryst. 3. 400. 1950

## Die Ergebnisse der Aufnahme sind folgende:

2 $\theta$	d <sub>hkl</sub> (Å)	Intensität	Indizes	2 $\theta$	d <sub>hkl</sub> (Å)	Intensität	Indizes
8,94	9,91	st	002	42,46	2,130	m	043
17,88	4,96	m	004	44,90	2,018	s.sch	0.0.10
19,89	4,46	s.st	110	46,10	1,969	s.sch	206
22,84	3,89	sch	113	47,77	1,904	sch	046
24,08	3,70	sch	023	52,08	1,757	sch	138
25,45	3,50	m	114	53,93	1,700	s.sch	208
26,84	3,32	m	006, 024	55,73	1,649	s.sch	1.3.10
31,50	2,84	sch	115	56,47	1,630	sch	312
33,33	2,688	sch	—	57,78	1,596	s.sch	313
34,99	2,564	s.st	202	61,87	1,500	st	060
36,59	2,456	sch	133	69,48	1,353	sch.d	335
37,90	2,374	sch	133	73,02	1,296	m	400
40,26	2,240	s.sch	221	76,61	1,244	sch	0.0.16
40,99	2,202	s.sch	223				

	a <sub>0</sub>	b <sub>0</sub>	c <sub>0</sub>	c <sub>0</sub> sin $\beta$	$\beta$
Muskovit	5,18	9,02	20,04	—	95°30'
Hydromuskovit von Ogofau	5,185	9,025	—	20,20	—
Hydromuskovit von Nagyörzsöny	5,20	9,00	20,00	19,92	95°3'
Illit	5,20	9,00	—	19,90	—
Kaolinit	5,14	8,90	7,37	—	91°8'
Montmorillonit	5,10	8,83	15,20	—	90°
Pyrophyllit	5,14	8,90	18,55	—	99°55'

Aus der Tabelle ist ersichtlich, daß man es hier mit einem, dem Muskovit nahestehenden Hydroglimmer (Hydromuskovit oder Illit) zu tun hat. Unter den Linien befinden sich auch charakteristische Illitlinien.

Aus dem Molekulargewicht und den Angaben der Elementarzelle wurde das spezifische Gewicht (G) des Tonminerals von Nagyörzsöny und von Ogofau nach der bekannten Formel berechnet, die zum Vergleich mit den Angaben des spezifischen Gewichtes des Muskovits und des Hydromuskovits von Ogofau mitgeteilt wird.

	G (berechnet)	G (gemessen)
Muskovit	2,78—2,88	
Hydromuskovit von Ogofau [9]	2,70	2,65 $\pm$ 0,02
Hydromuskovit von Nagyörzsöny	2,81	—

Die sich aus der röntgenographischen Untersuchung ergebende Voraussetzung, das Tonmineral von Nagybörzsöny könnte auch Illit sein, wurde durch die DTA-Untersuchung desselben, die V. KOBLENCZ durchführte, widerlegt. Wie bekannt, verlieren die Tonminerale ihren Wassergehalt, der in den einzelnen in verschiedenen Bindungsenergien vorhanden ist, im Laufe der Differential-Thermoanalyse bei verschiedenen Temperaturen. Der Wasserverlust unter  $300^{\circ}$  ist nicht mit der Umwandlung des Silikatgerüsts verbunden, während über  $500^{\circ}$  die Wasserabgabe meistens zugleich die tiefgreifende Veränderung des Gerüsts nach sich zieht. Die das Entweichen des Koordinationswassers und Strukturwassers andeutenden Endothermspitzen sind bezeichnend für die einzelnen Tonminerale. So haben Illit und Montmorillonit je zwei charakteristische Endothermspitzen; die erste liegt bei beiden zwischen  $100$  und  $250^{\circ}$ , die zweite erscheint beim Montmorillonit um  $700^{\circ}$ , während sie sich beim Illit zwischen  $500$ — $600^{\circ}$  zeigt. Ferner haben beide, meistens um  $900^{\circ}$ , eine Endotherm-Exothermdoppelspitze, die die nach dem Verlust des gesamten Wassers eintretende Strukturveränderung anzeigt. Bei dem Normalmuskovit beobachtet man entweder keine Endothermspitzen, oder gegebenenfalls nur über  $700^{\circ}$ , während sie bei dem Pyrophyllit um  $800^{\circ}$  auftritt.

Zum Vergleich teilen wir die DTA-Kurven folgender Minerale mit (Fig. 1):

1. Muskovit (GRIM—ROWLAND) [21]
2. Serizit, Naurod, Taunus (V. KOBLENCZ)
3. Pyrophyllit, Beresowsk (V. KOBLENCZ)
4. Pyrophyllit, North Carolina (GRIM—ROWLAND) [21]
5. Damourit, Stoneham, Maine (V. KOBLENCZ)
6. Paragonit, Faïdo, Tessin (V. KOBLENCZ)
7. Paragonit, Fenestrella, Borgofranco (BARSHAD : „C“) [22]
8. Hydromuskovit, Nagybörzsöny I. (V. KOBLENCZ)
9. Hydromuskovit, Nagybörzsöny II. (V. KOBLENCZ)
10. Illit, Sárospatak (GRIM) [1]

Vom Hydromuskovit aus Ogofau haben BRAMMALL und Mitarbeiter keine DTA-Untersuchung veröffentlicht [9].

Aus den Kurven ist ersichtlich, daß der bekannte Serizit von Naurod keine Endothermspitze gibt zum Beweise dessen, daß er ein feinkörniger Muskovit ist. Die bei  $575^{\circ}$  wahrnehmbare Spitze deutet die Umwandlung des, den Serizit begleitenden,  $\beta$ -Quarzes zu  $\alpha$ -Quarz an. Mit den Kurven des Pyrophyllits, Muskovits und Damourits (eine Muskovit-Varietät) sind die Kurven des Hydromuskovits von Nagybörzsöny nicht zu identifizieren. Beim Illit von Sárospatak liegt die erste Endothermspitze zwischen  $100$ — $200^{\circ}$ , die zweite erscheint dagegen zwischen  $500$ — $600^{\circ}$ . Die Hydromuskovitproben von Nagybörzsöny haben je eine Endothermspitze zwischen  $600$ — $700^{\circ}$  und eine kleinere bei  $900$ — $1000^{\circ}$ . Wenn man die schwache, von Kalzitverunreini-

gung stammende Endothermspitze der Probe I um  $800^{\circ}$  und die beiden durch Verbrennen des Pyrits und Arsenopyrits verursachten Exothermspitzen der Probe II außer acht läßt, so kann man die Kurven von Nagyörzsöny mit der Paragonitkurve von J. BARSHAD [22] parallelstellen. Wie bei den beiden Proben des Hydromuskovits von Nagyörzsöny, so ist auch beim Illit von Sáropatak die dritte Endothermspitze bei  $900^{\circ}$  zu beachten. Aus dem Ver-

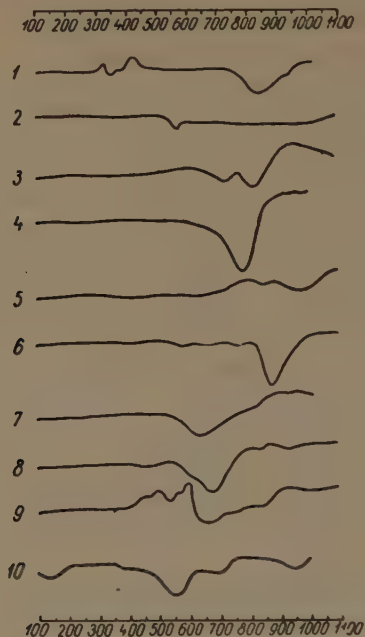


Fig. 1

gleich der Kurven ist ersichtlich, daß das Tonmineral von Nagyörzsöny kein Illit und kein Muskovit ist.

Vergleicht man endlich die Brechungsindizes des Muskovits [23], der Hydromuskovite von Ogofau [9] und Nagyörzsöny, sowie NAGELSCHMIDT's Angaben über die Brechungsindizes des Illits [24], so sieht man sogleich, daß es sich hier wirklich um Hydromuskovit und um keinen Muskovit oder Illit handelt, obwohl die Übereinstimmung der Gitterkonstanten auffallend ist.

	$\alpha$	$\beta$	$\gamma$
Muskovit (23).....	1,552	1,582	1,588
Illit von S. Wales (24) .....	1,572	1,587	1,600
Hydromuskovit von Ogofau (9) .....	—	1,575	1,580
Hydromuskovit von Nagyörzsöny .....	—	1,575	1,583



Auf Grund des Gesagten ergibt sich, daß man das Vorhandensein eines neuen Glimmerminerals, des sechsten Serizit-Minerals annehmen muß. Das neue Glimmermineral ist der *Hydroparagonit*.

Zum Ausgangspunkt dienten BARSHAD's Paragonit-Untersuchungen [22]. Er teilte die DTA-Untersuchungen [22] von zwei, aus verschiedenen, bekannten Fundorten stammenden »Paragonite« mit. In seiner Abhandlung, wie schon oben erwähnt, stimmt die mit »C« bezeichnete DTA-Kurve mit jener der Probe I des Hydromuskovits von Nagybörzsöny fast überein, der Endothermpunkt liegt bei 700°. An der mit »E« bezeichneten Paragonitkurve von BARSHAD erscheint die Endothermspitze um 800°. Autor beruft sich in seiner Abhandlung auf die Arbeit von SCHALLER und STEVENS [25], die die chemischen Analysen der beiden »Paragonite« ausführten. SCHALLER und STEVENS teilen jedoch die Analysenergebnisse nicht mit, sie weisen vielmehr auf die in DANA's »System of Mineralogy« (6. Ed. Seite 623.) mitgeteilten Analysen hin.

Demgemäß ist der Fundort des mit »C« bezeichneten »Paragonit's« (Cossait) von BARSHAD: Fenestrella bei Borgofranco, Valle del Chisone, Piemont, Italien. Nach SCHALLER und STEVENS ist das Mineral feinkörnig, von Serizit äußerem und seine Analysendaten stimmen mit jener, in Dana's Werk mitgeteilten Analyse No. 5. überein.

Der Fundort des mit »E« bezeichneten »Paragonit's« von BARSHAD ist: Monte Campione, Faido, Tessin, Schweiz. Seine Analysenergebnisse entsprechen der Analyse No. 1 in DANA's Werk.

Mit dem Paragonit vom Fundort Faido, Tessin, führte auch V. KOBLENCZ eine DTA-Kurve aus, sie ist die besprochene Kurve No. 6. Der Endothermpunkt liegt zwischen 800—900°, während er sich in BARSHAD's Untersuchungen um 800° zeigt. Die zwei Untersuchungen stimmen gut überein.

Die mit »C« bezeichnete Kurve weicht aber wesentlich von diesen ab. In Betracht ziehend, daß diese letztere mit der Kurve des Hydromuskovits von Nagybörzsöny übereinstimmt, liegt der Gedanke nahe, daß der sogenannte »Paragonit« (Cossait) von Fenestrella ebenfalls ein Hydroglimmer ist. Auf Grund der in Dana's Werk mitgeteilten Analysendaten haben wir die Ionenzahlen beider Minerale berechnet.

Die Ergebnisse der Analysen sind folgende :

I. Fenestrella, Borgofranco :

SiO <sub>2</sub>	46,67%
Al <sub>2</sub> O <sub>3</sub>	39,02%
Fe <sub>2</sub> O <sub>3</sub>	2,01%
K <sub>2</sub> O	1,36%
Na <sub>2</sub> O	6,37%
H <sub>2</sub> O	4,91%
	<hr/> 100,34%

II. Monte Campione, Faido, Tessin :

SiO <sub>2</sub>	46,81%
Al <sub>2</sub> O <sub>3</sub>	40,06%
Fe <sub>2</sub> O <sub>3</sub>	Sp.
MgO	0,65%
CaO	1,26%
K <sub>2</sub> O	Sp.
Na <sub>2</sub> O	6,40%
H <sub>2</sub> O	4,82%
	<hr/> 100,00%

## Die Ergebnisse der Berechnung sind :

## I. Fenestrella:

	%	Atomquotiente	Ionenzahlen	Ionenzahlen (O + OH = 12)
Si .....	21,81	0,7771	777,1	2,98
Al .....	20,66	0,7659	765,9	2,94 { 1,02 } <sup>4</sup>
Fe :::	1,41	0,0252	25,2	{ 1,92 } 2,01
Na .....	4,73	0,2057	205,7	0,09
K .....	1,13	0,0289	28,9	0,79 { 0,11 } 0,9
OH .....	9,28	0,5453	545,3	3128 { 2,09 } 12
O .....	41,32	2,5825	2582,5	{ 9,91 }

## II. Monte Campione:

	%	Atomquotiente	Ionenzahlen	Ionenzahlen (O + OH = 12)
Si .....	21,87	0,7794	779,4	2,97
Al .....	21,21	0,7863	786,3	3,00 { 1,03 } <sup>4</sup>
Mg .....	0,39	0,0161	16,1	{ 1,97 } 2,03
Ca .....	0,90	0,0225	22,5	0,06
Na .....	4,75	0,2065	206,5	0,09 { 0,88 }
OH .....	9,10	0,5351	535,1	0,79
O .....	41,78	2,6112	2611,2	3146 { 2,04 } 12
				{ 9,96 }

Aus den Ionenzahlen ist ersichtlich, daß das Mineral von Fenestrella wirklich ein Hydroglimmer ist, denn sein OH-Gehalt mit ungefähr 0,1 Äquivalent ist höher, als jener des Normal-Paragonits, während der OH-Überschuß beim Glimmer von Mte. Campione innerhalb der Versuchsfehlergrenzen bleibt. Dieser ist also kein Hydroglimmer, sondern tatsächlich Paragonit. Ferner entspricht beim Hydroglimmer von Fenestrella dem 0,1 Äquivalent OH-Überschuß genau das Maß der der Abnahme der Alkalien, das hier gleichfalls 0,1 Äquivalent beträgt. Es ist also  $n = m$  in der allgemeinen Strukturformel des Hydromuskovits. Dadurch wird es verständlich, warum man an der DTA-Kurve des Glimmers von Fenestrella den Endothermpunkt bei 700° erhält, während sich beim Glimmermineral von Monte Campione der Endothermpunkt bei 800—900° zeigt. Der Hydroparagonit stimmt nämlich strukturell mit dem Hydromuskovit überein, während die Struktur des Paragonits jener des Muskovits entspricht und in derselben Weise geht auch ihr thermischer Zerfall vor sich.

Hier müssen wir des von F. A. BANNISTER »Brammallit« genannten [2] Glimmerminerals gedenken. Zitierter Verfasser teilt die vollständige Analyse des Minerals nicht mit, sondern nur die Daten bezüglich Kalium und Natrium. Auf dieser Grundlage, sowie auf Grund der Brechungsindizes und der Ergebnisse der röntgenographischen Untersuchung, betrachtet er das Mineral als Natronillit. Faßt man aber seine Auseinandersetzung näher ins Auge, so ergibt sich, daß das Mineral keinesfalls als eine Illitart betrachtet werden kann, denn.

1. seine Korngröße ist nicht von kolloidaler Dimension, sie kann auch eine Grösse von 0,5 mm erreichen,
2. wird das Mineral bis 700° erhitzt, so verändern sich die röntgenographischen Daten nicht.

BANNISTER zieht daraus den Schluß, daß sich der Basenabstand, wie beim Montmorillonit, durch Wasserabgabe nicht vermindert. Es wurde im vorhergehenden bereits erwähnt, daß sowohl der Montmorillonit, wie auch der Hydromuskovit den überwiegenden Teil ihres Koordinationswassers während der DTA-Untersuchung bei 700° verlieren, während die Abgabe des Koordinationswassers bei den Illitarten schon bei 500—600° eintritt. Demnach ist also der Brammallit nicht zu den Illiten zu zählen, sondern auf Grund seines K : Na Verhältnisses, seiner Korngröße und seines Verhaltens bei Erhitzung ebenfalls als ein Hydroparagonit zu betrachten. Die Übereinstimmung der Gitterkonstanten mit jenen des Illits ist, wie man dies bei dem Hydromuskovit von Nagybörzsöny sah, kein entscheidender Untersuchungswert.

Im Sinne des Gesagten, vergleichen wir die in BANNISTER's Arbeit mitgeteilten Gitterkonstanten und Brechungsindizes mit den entsprechenden Daten des Hydromuskovits von Nagybörzsöny in der untenstehenden Tabelle (siehe auch oben S. 180.):

Die Werte für Paragonit beziehen sich auf jenen von Monte Campione, der, wie wir sahen, tatsächlich Paragonit, und kein Hydroparagonit ist. Die entsprechenden Daten des Hydroparagonits von Fenestrella sind nicht bekannt, aber auch die bisher bekannten liefern genügende Beweise für das Vorhandensein des Hydroparagonits, während das Bestehen des Natronillits auf Grund der Daten des »Brammallit« genannten Glimmerminerals als nicht erwiesen scheint.

	$a_0$	$b_0$	$c_0 \sin \beta$	$\alpha$	$\beta$	$\gamma$
Paragonit (2) .....	5,12	8,87	18,95	—	—	1,605
Brammallit (2) .....	5,2	9,00	19,2	1,561	—	1,579
Illit (2) .....	5,2	9,00	19,9	1,572	1,587	1,600
Hydromuskovit (Nagybörzsöny) .....	5,2	9,00	19,92	—	1,575	1,583
Hydromuskovit (Ogofau) (9)	5,19	9,03	20,02	—	1,575	1,580
Muskovit (2) .....	5,18	9,02	19,95	1,5628	—	1,5988

*Nachtrag während der Korrektur*

Während der Korrektur ist die 3. Auflage der Mineralogischen Tabellen von *H. Strunz* eingetroffen. *Strunz* reiht den Brammallit in dieser Arbeit (S. 307–308) sich auf Bannisters zitierte Abhandlung berufend unter den Namen Hydroparagonit, obwohl diese Benennung bei Bannister nicht zu finden ist. Nach seiner Feststellung: »*Hydromuskovite* von Tonteilchengröße werden in neuer Zeit bevorzugt als *Illite* bezeichnet: sie besitzen offenbar vorzugsweise 1Md-Struktur, sind also einschichtig-monoklin desorientiert.« Nach ihm: »Brammallit entspricht einem *Natrium-Illit*.« Er behandelt die Namen Hydroparagonit und Hydromuskovit als Sammelnamen.

Er gibt die Gitterkonstanten des Hydromuskovits mit annähernder Genauigkeit, wie folgt:

$$a_0 \sim 5,2 \quad b_0 \sim 9,0 \quad c_0 \sim 2 \cdot 10,0 \quad \beta \sim 96^\circ$$

Nach den Berechnungen von J. Erdélyi sind die Gitterkonstanten des Hydromuskovits:

$$a_0 = 5,2 \quad b_0 = 9,0 \quad c_0 = 20 \quad \beta = 95^\circ 3'$$

Die 3. Auflage des Werks von *Strunz* ist am 1-sten August 1957. erschienen, während J. Erdélyi seine Arbeit am 6-sten Mai 1957. an der Sitzung des Geochemischen Hauptausschusses der Ungarischen Akademie der Wissenschaften vorführte.

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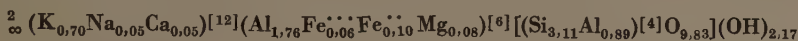
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## HYDROPARAGONITE, A NEW MICA MINERAL, AND ITS RELATIONS TO HYDROMUSCOVITE, NATRONILLITE AND BRAMMALLITE

J. ERDÉLYI, V. KOBLENCZ and V. TOLNAY

### Abstract

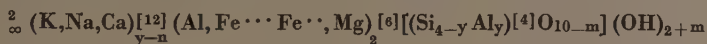
1. The clay mineral of Nagybörzsöny is a hydromuscovite related to muscovite, on the basis of Analysis No. 1 its special structural formula is as follows:



2. This hydromuscovite as well as the ore vein associated with it are of mesothermal origin. The hydromuscovite of Nagybörzsöny is in a closer relation to muscovite than the occurrence of Ogofau, which is of epithermal origin [9].

3. In the hydromuscovite the O-ions of the tetrahedral sheet are substituted by OH-surplus, consequently the quantity of alkali metal ions decreases. The quantity of O-ions in the tetrahedral sheet decreases to such an extent, as the equivalent number of OH-ions increases.

Thus the general structural formula of hydromuscovite is as follows:



Further investigations are needed to establish whether there exists the relationship  $n = m$ , which could be clearly demonstrated in case of the hydroparagonite of Fenestrella.

4. In comparing the results of our investigations with the data obtained by other authors the existence of a new mica mineral, viz. hydroparagonite could be ascertained with certainty.

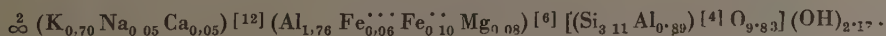
5. The mineral described under the name brammallite must be considered as hydroparagonite and not as natronillite. The existence of natronillite does not seem to be confirmed.

О НОВОМ СЛЮДЯНОМ МИНЕРАЛЕ ГИДРОПАРАГОНИТЕ, А ТАКЖЕ О ЕГО ОТНОШЕНИЯХ С ГИДРОМУСКОВИТОМ, НАТРОНИЛЛИТОМ И БРАММАЛЛИТОМ

Й. ЭРДЕЛЫИ, В. КОБЛЕНЦ и В. ТОЛЬНАИ

### Резюме

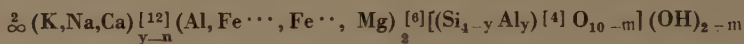
1. Глинистый минерал, обнаруженный в районе с Надьбёржён, представляет собой близкий к мусковиту гидромусковит, формула строения которого на основании анализа № 1 может быть написана следующим образом:



2. Происхождение указанного гидромусковита, а также сопровождающей им жилы является мезотермальным. Гидромусковит с. Надьбёржён располагается ближе к мусковиту, чем месторождение эпитеермального происхождения с. Огофау [9].

3. В гидромусковите место О-ионов тетраэдрового слоя занимает ОН-избыток, вследствие чего количество щелочно-металльных ионов, обладающих реакционной способностью, уменьшается. Количество О-ионов тетраэдрового слоя уменьшается настолько, насколько повышается эквивалентное количество НО-ионов.

Общая формула гидромусковита таким образом является следующей:



При помощи дальнейших исследований и тщательных анализов необходимо установить, существует ли зависимость  $n = m$ , которая в связи с гидропарагонитом района Фенестрелла была четко обнаружена.

4. На основании сравнения результатов наших исследований с данными исследований других авторов существование нового слюдяного минерала — гидропарагонита было установлено без сомнения.

5. Минерал, описанный под названием браммаллита, следует считать не натронилитом, а гидропарагонитом. Существование натронилита пока не является доказанным.

# ESSAI SUR LA DÉTERMINATION DES CHALEURS DE DISSOCIATION DES MINÉRAUX

Par

M. FÖLDVÁRI-VOGL et B. KLIBURSZKY

INSTITUT GÉOLOGIQUE DE HONGRIE ET UNIVERSITÉ EÖTVÖS, BUDAPEST

Nous avons déterminé des chaleurs de dissociation de quelques minéraux à l'aide de l'analyse thermique différentielle et par un microcalorimètre construit spécialement à cette fin. On a cherché un rapport théorique entre les résultats respectifs, obtenus par les deux méthodes de détermination et on a essayé de convertir mutuellement les deux séries de résultats. Nous espérons que, par le développement de nos résultats calorimétriques, nous pourrions obtenir la mesure de la force de liaison du radical OH des minéraux.

Les analyses thermiques différentielles permettent de déterminer les changements produits dans la quantité de chaleur lors de la dissociation des minéraux, ce qui est bien démontré dans les articles de M. WITTELS, I. BARSHAD et G. SABATIER [1, 2, 3, 4]. Notamment le crochet thermique indiquant la dissociation du minéral est en fonction, outre de la quantité présente du minéral en question, de la chaleur produite (ou absorbée). Quand même, on est d'avis que cette question est encore incertaine. En effet, il y a des différences remarquables entre les résultats des mesures, donnés par les divers auteurs. P. e. il est frappant que la valeur de 600° C environ de la chaleur de dissociation, mesurée lors de l'altération de la kaolinite, correspond selon la détermination de BARSHAD à 253 cal/g, tandis que selon SABATIER à 111 cal/g. La contradiction est souvent très considérable, même dans le cas d'autres minéraux.

Nous avons soumis à une investigation systématique l'examen des facteurs et des sources d'erreurs qui peuvent influencer sur les déterminations de chaleur de dissociation, accomplies à l'aide de l'analyse thermique différentielle.

Les erreurs sont bien connues, pour la plupart, en connexion avec l'examen de l'applicabilité de l'analyse thermique différentielle aux déterminations quantitatives. Ce sont les mêmes facteurs qui influent aussi sur la forme et l'étendue de l'aire du crochet. En premier lieu, la forme de l'aire du crochet dépend de la vitesse de chauffage du four de l'appareil d'analyse thermique différentielle. Théoriquement, on pourrait supposer que par l'augmentation de la vitesse de chauffage, on n'obtienne qu'un crochet à plus grande amplitude qui soit proportionnellement plus étroite, et que, par conséquent, l'aire du crochet ne dépende pas de la vitesse du chauffage, mais,

malheureusement, cette supposition ne fut pas entièrement prouvée par l'expérience. WITTELS (1. c.) a examiné en détail ce problème et il a tracé une relation graphique entre la vitesse de chauffage et l'aire du crochet. La forme et, quelque peu, même l'étendue de l'aire du crochet dépendent des grandeurs granulométriques du minéral en question. Quand même, la question se pose si l'aire du crochet change avec la grandeur granulométrique parce que la valeur de la chaleur de dissociation soit dépendante, dans une certaine mesure, des grandeurs granulométriques du minéral.

La mesure de l'aire du crochet peut devenir erronée s'il n'est pas possible de délimiter l'aire du crochet sans équivoques, par le prolongement de la ligne de base. Cela arrive quand, après le crochet, la ligne de base ne retourne

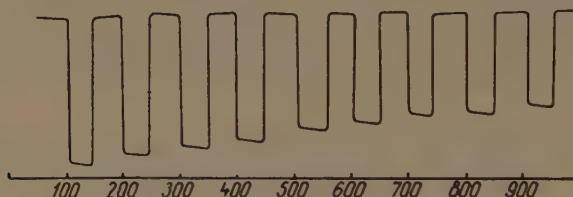


Fig. 1

pas précisément à sa place initiale. Même en dépit de l'application des solutions graphiques recommandées pour ces cas-là, on peut commettre une erreur relative de 5 à 10% lors de la mesure des quantités de chaleur.

SABATIER attire notre attention sur un fait très important ; notamment il faut reconnaître que la relation entre l'aire du crochet et la quantité de chaleur, c'est-à-dire la valeur cal/aire du crochet n'est pas indépendante de la température où la dissociation s'accomplit. Pour cette fin, SABATIER a choisi des substances qui se dissocient à températures diverses et dont la chaleur de dissociation est bien connue de la littérature et il a obtenu une courbe d'étalonnage pour déterminer la valeur de cal/aire du crochet en fonction de la température.

Sa courbe d'étalonnage est presque linéaire et elle prouve qu'au fur et à mesure qu'on élève la température, les aires de crochet appartenant à la même quantité de chaleur, deviennent plus petites.

Avant d'aborder le problème des déterminations de la quantité de chaleur, nous voulons traiter en détail les points de vue quantitatifs de ce dernier facteur. Pour examiner cette question, on a employé la solution suivante :

Dans chacun des creusets du porte-échantillon de notre appareil d'analyse thermique différentielle, nous avons placé de la substance inerte. D'ailleurs, le fonctionnement et le branchement de notre installation étaient



ceux qu'on emploie habituellement [5]. Nous avons chauffé le four à une vitesse de 100° C/6 minutes, de la température ambiante à 1000° C. Dans la substance inerte placée dans l'un des creusets, nous avons noyé un filament spiral de chauffage (5,6  $\Omega$  de résistance) et nous avons fait passer par ce petit filament spiral un courant de 0,68 A d'intensité, à des intervalles réguliers à chaque 100° C environ, pour une durée de 3 minutes exactes. Après 3 minutes, nous avons interrompu le courant du petit filament spiral et nous l'avons fermé de nouveau après l'élévation suivante de 100° C de la température. Le galvanomètre branché sur les couples thermiques différentielles placées dans les deux creusets a enregistré les chaleurs produites dans le filament spiral et il a tracé des aires de déviation (v. fig. 1.).

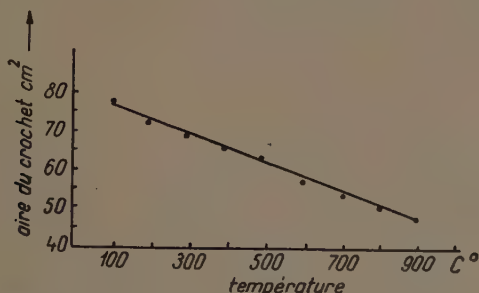


Fig. 2

Comme on voit clairement à la figure, les aires limitées par les déviations du galvanomètre diminuent vers les températures élevées. C'était sur cette diminution d'aire que nous avons calculé la proportion entre la calorie et l'aire du crochet, à une température donnée (fig. 2).

Sur la base de ces considérations, nous avons calculé les chaleurs de dissociation de quelques minéraux, sur l'aire du crochet d'analyse thermique différentielle et nous avons obtenu les résultats suivants :

Minéral	Chaleurs de dissociation mesurées cal/g des aires des crochets
Gypse (pro anal.)	170
Kaolinite (Zettlitz)	106
Hydrargyllite (Istrie)	220
Carbonate de magnésium (pro anal.)	320

Ces résultats s'accordent en gros avec les valeurs données par SABATIER aussi [4], mais la précision ne peut pas être considérée comme suffisante, ni par rapport aux données trouvées dans la littérature, ni par comparaison avec nos déterminations parallèles.

Vu ces difficultés, nous avons essayé de mesurer les chaleurs de dissociation à l'aide d'une méthode différente. A cette fin, nous avons construit une petite installation calorimétrique. En substance, notre installation consiste à chauffer le minéral par la voie électrique, dans un système calorimétrique calorifugé et mesurer la quantité de chaleur récupérée durant le processus de refroidissement. La différence entre les deux valeurs d'énergie donne la quantité de chaleur consommée au cours de la dissociation thermique du minéral (en cas d'un processus endothermique). Naturellement la chaleur de dissociation obtenue de cette façon-là n'est pas identique à la quantité de chaleur représentée par le crochet thermique. On reconnaît facilement ce fait si l'on suit de pas à pas les processus thermiques qui se déroulent dans le calorimètre pendant un cycle entier de chauffage-refroidissement et, d'autre part, durant la formation du crochet de la courbe thermique différentielle. D'abord, on examinera ce processus en connexion avec la dissociation d'un minéral contenant du radical OH.

Après avoir placé la poudre du minéral dans un petit four électrique, on la met dans le calorimètre. (V. la description de l'installation, plus bas.) On réchauffe le minéral à l'aide du courant électrique jusqu'à la température où le processus de la dissociation thermique se sera sûrement accomplie. On mesure d'une manière précise la quantité de chaleur  $Q$ , nécessaire au chauffage. Puis, on mesure la quantité de chaleur transmise par le minéral à son ambiance, dans le calorimètre. En général, les deux chaleurs ne sont pas égales; notamment, en cas d'un processus endothermique, on récupère moins de chaleur après le refroidissement de la substance que la quantité de la chaleur dépensée au réchauffement, la différence étant consommée par le processus de la dissociation. En divisant le processus de réchauffement et refroidissement en processus partiels, on peut indiquer les pas suivants:

1°. Une quantité de chaleur  $q_1$  est nécessaire à réchauffer le minéral non-altéré, de la température de départ ( $t_0$ ) à la température initiale de l'altération thermique, cette quantité étant évidemment le produit de la multiplication de la chaleur spécifique et de la masse de la substance par la différence de température:

$$q_1 = m \cdot c_1 (t - t_0)$$

2°. Une partie du reste de la chaleur ( $q_2$ ) est dépensée durant le processus de la dissociation thermique, à la libération des radicaux OH, sous la forme de vapeur, du lattis, puis au changement produit dans l'énergie intérieure du lattis. Le chauffage est fini par là.

Les processus partiels du refroidissement sont les suivants:

3°.  $q_3$  est la quantité de chaleur transmise par la substance déshydratée à son ambiance, pendant le refroidissement à la température ambiante: (Cette

quantité n'est pas identique à  $q_1$ , car la chaleur spécifique et la masse de la substance ont changé, par suite de la dissociation.)

$$q_3 = m_2 c_2 (t_1 - t_0)$$

4°. Le refroidissement de la vapeur produite par la dissociation du minéral, de la température  $t_1$  à  $100^\circ$  C. On désigne par  $q_4$  la chaleur libérée par ce processus.

5°.  $q_5$  est la quantité de chaleur libérée lors de la condensation de la vapeur, à  $100^\circ$  C.

6°. Le refroidissement de l'eau liquide, de  $100^\circ$  C à la température ambiante ; la chaleur libérée pendant ce processus est désignée par  $q_6$ .

En résumant les processus partiels, la différence des quantités de chaleur transmises au système et récupérées peut être exprimée de la façon suivante :

$$Q - \Delta Q = Q - (-q_1 - q_2 + q_3 + q_4 + q_5 + q_6),$$

soit

$$\Delta Q = -q_1 - q_2 + q_3 + q_4 + q_5 + q_6.$$

Cependant, si la détermination est faite sur la base de la courbe thermique, la quantité de chaleur représentée par l'aire du crochet ne correspond qu'à  $q_2$  de parmi les processus partiels que nous venons de décrire en détail. Pourtant, si l'on connaît la chaleur spécifique du minéral en question, les résultats obtenus à l'aide des deux méthodes sont mutuellement convertibles.

En ce qui suit, nous donnons la description de notre calorimètre, puis nous rendons compte de quelques résultats, et, en connexion avec ceux-ci, nous employons notre considération théorique à des cas concrets.

On place la substance examinée dans un petit four électrique cylindrique, de 10 mm de diamètre et 16 mm environ de hauteur. Le filament de chauffage du four se trouve à la surface intérieure du four et ainsi il est en contact direct avec l'échantillon soumis à l'examen, par là le réchauffement rapide de l'échantillon est assuré. La matière du filament est *Kanthal A.*, de 0,8 mm de diamètre. Le four est réchauffé par un courant alternatif dont le voltage est de 12 V, l'intensité étant de 5 A. De l'extérieur, la bobine de chauffage est entourée par un isolateur en asbeste qui, à son tour, est supporté par un manchon extérieur en nickel. Une couple thermique Pt-Pt rhodié est centrée dans le petit four, à l'aide d'un tube de porcelaine à double forure.

Notre four électrique est placé au milieu d'un petit vase dévissable en forme de bombe calorimétrique. Nous avons plongé notre bombe calorimétrique dans 200 ml d'eau contenue dans un vase en cuivre rouge ; le système entier a été multiplement calorifugé de dehors, selon la manière habituelle des mesures calorimétriques. Un mince capillaire en cuivre s'avance dans l'espace intérieur de la bombe calorimétrique ; ce capillaire long de 50 cm

environ fut ployé en filets multiples, le long du paroi de la bombe calorimétrique. C'est ce capillaire en cuivre qui conduit vers l'extérieur les gaz produits durant la dissociation, mais vu que le gaz doit suivre un cours long dans l'eau du calorimètre, on obtient que le gaz sortant est refroidi à la température de l'eau et ainsi il ne cause pas de perte de calorie par son départ. Le départ des gaz assure que la dissociation soit accomplie à une pression de l'atmosphère. On observe la température de l'eau dans le calorimètre de la manière habituelle, par un thermomètre Bockman, à chaque demi-minute ou minute.

La détermination est faite de la façon suivante : après avoir observé une période antérieure convenable, on ferme le circuit du four et on mesure la quantité du courant par un compteur. Le circuit sera fermé jusqu'à ce que l'instrument de la couple thermique noyée dans l'échantillon soumis à l'examen indique une température où le processus de dissociation à examiner se soit sûrement accomplie. L'observation de cette température est d'autant plus facile que l'instrument de la couple thermique s'arrête à la température de la dissociation, jusqu'à l'accomplissement total de la dissociation et puis il recommence à s'élever très rapidement. La dose de l'échantillon était en général de 0,6 à 0,8 g. Le réchauffement ne prend que 1 ou 2 minutes, au fur et à mesure de la température de dissociation. Puis, en interrompant le courant du four, on observe le réchauffement de l'eau du calorimètre et, après l'accomplissement de la compensation thermique, on mesure la période ultérieure, de la manière habituelle.

Si, au lieu de l'échantillon à examiner, on place une substance thermiquement inerte dans notre petit four, en cas d'un chauffage par le même wattage, le réchauffement de l'eau du calorimètre atteint évidemment une valeur plus élevée que lors de l'examen d'une substance dont la dissociation est accompagnée d'un processus endothermique. Sur la base de la différence entre les deux valeurs, on peut déterminer, de la façon décrite plus haut, la quantité de chaleur consommée par la dissociation, désigné plus haut par  $4Q$ .

Après avoir surmonté les difficultés initiales, nous avons réussi à diminuer l'erreur maximum de nos déterminations à 2 ou 3 calories. Ayant accompli les déterminations, nous nous sommes efforcés de contrôler — par la détermination de l'éventuelle diminution de poids, produite par le réchauffement répété de l'échantillon retiré — si le processus de la dissociation s'est véritablement déroulé dans le calorimètre. Chacun de nos résultats est la moyenne d'au moins 5 ou 6 déterminations parallèles.

Comme premier essai, nous avons principalement examiné des minéraux à hydroxyle (kaolinite, hydrargyllite, boehmite, diasporé), mais, à titre de comparaison, nous avons aussi mesuré la chaleur de transformation du gypse, en outre nous avons cherché un exemple de la dissociation des carbonates, par la détermination de la chaleur de dissociation de la magnésite.



Voici un tableau synoptique des moyennes des résultats de nos examens :

Échantillon	Perte de chaleur, mesurée dans le calorimètre : $\Delta Q$ cal/g
Kaolinite .....	98
Diaspore.....	73
Boehmite .....	68
Hydrargyllite .....	80 à 100
Gypse .....	34
Carbonate de magnésium .....	319

Parmi ces échantillons-là, le gypse et le carbonate de magnésium sont des produits chimiques de qualité «pro analysis». Dans le cas des autres minéraux, nous sommes partis des occurrences aussi pures que possible, p. e. de la kaolinite de Zettlitz, de l'hydrargyllite d'Istrie, du diaspore de Banská Bela. En chaque cas, nous avons déterminé par la voie chimique la teneur en minéral pur de l'échantillon examiné pour y rapporter les résultats. C'est la boehmite qui a causé le plus de difficulté. A cette fin, nous avons choisi un échantillon de bauxite dont la teneur en kaolinite était insignifiante mais dont le minéral bauxitifère dominant était la boehmite et qui — d'après l'analyse thermique différentielle et l'examen aux rayons X — ne contient d'hydrargyllite qu'en traces ; la teneur en fer n'étant pas représenté par la limonite mais par l'hématite. Ainsi, outre la boehmite, l'échantillon ne contient pas d'autre minéral dont la dissociation est accompagnée de déshydratation. C'était un échantillon de bauxite de Halimba-Tamáskút (pris par Gy. BÁRDOSY) qui nous a semblé le plus propre à cette fin. Nous avons dosé la teneur en boehmite de l'échantillon.

Parmi les valeurs de  $\Delta Q$  ce sont celles d'hydrargyllite qui sont les plus dispersées. On a supposé que la grande quantité de vapeur se soit produite si rapidement que son départ par le capillaire ait été accompli avant d'être refroidie à la température de l'eau du calorimètre. On traitera plus tard l'investigation de cette source d'erreur.

Quant à l'évaluation des résultats de nos examens, nous voulons insister sur les conclusions tirées de la comparaison entre les résultats calorimétriques et ceux d'analyse thermique différentielle. Il s'ensuit des considérations théoriques mentionnées plus haut que les valeurs de chaleur mesurées sur l'aire du crochet thermique et celles enregistrées par le calorimètre ne peuvent pas être identiques en cas d'un minéral dont la dissociation est accompagnée de dégagement de vapeur, car les résultats mesurés dans le calorimètre sont diminués par la quantité de chaleur nécessaire à la condensation de la vapeur durant le refroidissement. En effet, les valeurs  $\Delta Q$  mesurées par le calori-

mètre sont plus basses que celles qu'on obtient par l'analyse thermique différentielle. Il n'y a qu'une exception, notamment le cas de  $\text{MgCO}_3$  où les deux résultats concordent. Nous avons fait figurer  $\text{MgCO}_3$  parmi nos mesures justement pour prouver que la différence entre les deux sortes de résultats était due à la précipitation de la vapeur.

Sur la base des considérations que nous venons d'exposer, il est également évident que, si l'on veut tirer des conclusions quant à la force de liaison des radicaux OH dans le minéral, les résultats obtenus par calorimétrage sont plus proches de la réalité, car l'énergie d'évaporation de l'eau libérée n'y figure plus.

Dans cet ordre d'idées, la valeur calorimétrique basse  $\Delta Q$  du gypse n'est pas frappante, celle-ci indique, d'ailleurs, que la majeure partie de la chaleur de déshydratation du gypse, connue de la littérature, est consommée par l'évaporation de l'eau cristalline libérée et ce n'en est qu'une partie insignifiante qui est nécessaire à la libération de l'eau cristalline du lattis.

Enfin, dans le cas de deux minéraux, nous avons essayé de calculer, à partir de la valeur  $\Delta Q$  obtenue par calorimétrie, en tenant compte des considérations théoriques exposées plus haut, la valeur à attendre de la chaleur de dissociation mesurée sur la base de l'aire du crochet thermique. De parmi nos examens, nous avons choisi ces deux minéraux dont on trouve des constantes physiques authentiques dans la littérature.

Dans le cas du gypse, la valeur  $\Delta Q$ , obtenue par calorimétrie est de 34 cal. On a supposé que la température de dissociation était  $200^\circ \text{C}$ , la teneur en eau 21%, la chaleur spécifique du gypse 0,25, celle de l'anhydrite 0,18.

De la formule

$$\Delta Q = q_1 + q_2 - q_3 - q_4 - q_5 - q_6 :$$

$$\Delta Q = 34$$

$$q_1 = 1 \times 0,25 \times 180 = 45 \text{ cal.}$$

$$q_2 = \text{la chaleur mesurée par l'analyse thermique différentielle, en ce cas-ci c'est la valeur à calculer}$$

$$q_3 = 0,79 \times 0,18 \times 180 = 25,5 \text{ cal.}$$

$$q_4 = 0,21 \times 0,48 \times 100 = 10,1 \text{ ,,}$$

$$q_5 = 0,21 \times 540 = 113,5 \text{ ,,}$$

$$q_6 = 0,21 \times 80 = 16,7 \text{ ,,}$$

Par la substitution de ces valeurs :

$$q_2 = 150,8 \text{ cal.,}$$

ce qui s'accorde bien avec la chaleur de déshydratation connue de la littérature.

En effectuant les calculs d'une manière semblable, pour la kaolinite,

$$q_2 = 192 \text{ cal/g.}$$

Cette valeur est plus haute que celle qu'on obtient par l'analyse thermique différentielle, et par comparaison avec les données publiées dans la littérature, elle s'intercale entre la valeur donnée par BARSHAD et celle de SABATIER et elle ne diffère pas beaucoup de la valeur de 213 cal/g de la chaleur de dissociation, donnée par «Gmelin's Handbuch».

Il est difficile de soumettre notre méthode d'examen à une critique réelle tant qu'il y aura des différences si considérables entre les données disponibles des divers auteurs.

En ce qui concerne le développement de nos examens, nous sommes d'avis qu'il faut augmenter la précision des mesures calorimétriques et nous espérons de pouvoir donner, par là, des résultats pratiques informatifs sur la force de liaison des radicaux OH des minéraux.

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### VERSUCH DER BESTIMMUNG DER ZERSETZUNGSWÄRME VON MINERALEN

M. FÖLDVÁRI-VOGL und B. KLIBURSZKY

#### *Zusammenfassung*

Die Bestimmung der Zersetzungswärme von Mineralen wurde mit dem DTA-Verfahren und mit einem besonders zu diesem Zwecke konstruierten Mikrokalorimeter durchgeführt. Es wurde versucht, zwischen den bei der Anwendung der zweierlei Bestimmungsverfahren erzielten Resultate einen theoretischen Zusammenhang zu finden und die beiden Resultate ineinander umzurechnen. Durch Weiterentwicklung der kalorimetrischen Resultate hoffen wir für die Bindungsstärke der OH-Radikale von Mineralen eine Maßzahl erhalten zu können.

### ПОПЫТКА ОПРЕДЕЛЕНИЯ ТЕПЛОТЫ РАЗЛОЖЕНИЯ МИНЕРАЛОВ

М. ФЭЛЬДВАРИ-ФОГЛ и Б. КЛИБУРСКИ

#### *Резюме*

При помощи дифференциально-термического анализа и применением сконструированного для этой цели микрокалориметра была определена теплота разложения минералов. Между результатами, полученными при определении, проведенном двумя указанными способами, авторы искали теоретическую зависимость и пытались перевести результаты двоякого рода одни из других. От дальнейшего развития калориметрических результатов можно надеяться, что будут получены параметры связочной мощности ОН-радикалов различных минералов.





# ON THE PETROLOGY OF VOLCANIC ROCKS AND THE INTERACTION OF MAGMA AND WATER

By

E. SZÁDECZKY-KARDOSS

EÖTVÖS UNIVERSITY, BUDAPEST

In connection with recent investigations carried out in the Tertiary volcanic belt of the Carpathians, the author has pointed out the quite considerable effect of the coal and of moist sandy-clayey, marly and pyroclastic country rocks upon the magma. This effect, called transvaporization, fundamentally changes the chemical composition and trend of differentiation even of large magma bodies. Some rocks, as certain kinds of propylites, analcite-basalts, analcite-diabases, crinanites, teschenites, weilburgites, Lahn-keratophyres, alkali pegmatites, lugarites, analcite-syenites, further perlites, pitchstones, pumices, etc. are partly or entirely formed by the effect of this process. These rocks are not normal orthomagmatites but they are produced by considerable extension of the temperature interval of crystallization, up to the hydrothermal stage. It is proposed to denominate such rocks as hypomagmatites.

There are systematically described, on the other hand, subsequent alterations of volcanic rocks, and further, some new types of rocks of this kind, e. g. oxy metavolcanites, leucovolcanites, chlorovolcanites, hydrovolcanites and pseudoagglomerates.

The formation of these rocks is closely connected to the development of different joint systems of volcanic rocks. Thus the author attempts to describe the genesis of the latter ones.

The evaluation of these new concepts concerning the classification of magmatic rocks is also briefly described.

As this paper is an introduction to a synthetic interpretation of the complex investigation of (sub)volcanic mountains, it finally deals with the subsidence structure of volcanic mountains, as well as with the application of a new method to structural investigation of the same.

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In connection with our complex geological and geochemical investigations in the volcanic chain of the Carpathians, several problems related to the genesis of volcanic rocks were studied from the double point of view of the interaction of magma and water, viz. of igneous rock and water. These problems are connected with some difficulties of the interpretation of volcanic mountains partly elucidated by VADÁSZ, SERGEYEVSKY and TÖRÖK [1, 2, 3]. Such difficulties may be arranged as follows:

1. The comparative description of volcanic mountains is impeded by the lack of uniform concept, classification and nomenclature of the so-called

decomposed igneous rocks. 2. Observations concerning many "hydrated" igneous rocks can hardly be brought into accord with the generally accepted endogenetic derivation of magmatic water. 3. In many cases, the correlation between the rocks of volcanic mountains and the products of active volcanoes is doubtful. 4. The possibility of dip measurements, in volcanic mountains, is mostly lacking because of the large mass of lava-rocks and the frequently unstratified appearance of pyroclastites, consequently, the structure of volcanic mountains and its connection with the structure of active volcanoes are also often unsettled.

The present paper is a brief preliminary report on more extensive investigations concerning the elucidation of these difficulties. Particular results relating to special rock and ore types will be exposed in separate papers.

The present paper was elaborated on the basis of data collected partly by the author during his former, partly unpublished, investigations in the Hargita, Gutin, Avas and Szinyák Mountains and, on the other hand, in the course of recent surveys carried out in the company of his collaborators, principally with V. SZÉKY-FUX, further on J. KISS, F. KASZANITZKY, I. KUBOVICS, L. PESTY, Cs. RAVASZ, in the Tokaj, Mátra, Börzsöny and Dunazug Mountains. The main results were expounded at a conference of the Geochemical Committee of the Hungarian Academy of Science (November 4th and 5th, 1957), where the valuable remarks of E. VADÁSZ, A. FÖLDVÁRI, S. KOCH, L. TOKODY, F. HORUSITZKY, G. KERTAY G. PANTÓ, E. NEMETZ, E. SCHERF, K. BALOGH, B. JANTSKY, J. ERDÉLYI, M. HERRMANN, GY. VARJU, A. VIDACS, GY. MARTON also contributed to this work.

## I. Relation between magma and water

### *The phenomenon of transvaporization*

The mutual effect of the two phases, water and magma, is a problem of migration of elements. As for the migration of elements, we previously recognized two principal factors [4, 5]. In the case of slow processes the ionic density (Ionenwichte) and the bond strength [7] was found decisive for the migration of elements. These effects are traceable probably in the separation of some alkaline igneous provinces, further in the zoning of crystalline schists, and, according to recent investigations carried out by P. ESKOLA, in the process of granitization [6].

The interaction of magma and water belongs to the rapid processes. In this respect, the relation of the migrating phases may be expressed practically as follows. Volatile elements migrate from places of higher pressure towards those of lower pressure, i. e. from systems of higher tension and concentration of the migrating component towards those of lower tension and

concentration. Briefly, the migration of volatile elements takes place in the direction of the pressure slope. Therefore the migration of elements of lower potential and bond strength i. e. those of higher volatility is the most intense.

The contact of magma with water or water-containing country rocks, respectively, produces high-pressure vapour. After filling up the cavities and fissures of the country rocks, the water penetrates into the still liquid, consequently permeable and originally mostly lower-pressure magma, which partly resorbes it, in the shape of steam bubbles, and then gradually dissolves the vapour content of the latter ones. The melting temperature and viscosity of the magma are decreased thereby, consequently the physical condition of vapour resorption becomes more favourable and the duration of the whole process is increased.

This sort of hydration of the magma may be called *transhydratation*, or, taking into consideration other volatile substances, *transvaporization*. At higher pressure i. e. at greater depth, water being in the critical state, the increase in pressure becomes lower, consequently migration will become slower. However, the process is generally the same in the fluid phase as in the vapour phase.

Thus the migration of water chiefly does not take place in the direction of the temperature slope but on the contrary, from the cooler towards the higher-temperature medium. Temperature only activates this process.

Transvaporization takes place if 1. lava directly flows into water, or 2. it forms submarine eruptions, further, 3. when it flows upon moisture-containing (chiefly sedimentary) rocks or 4. it breaks through such rocks and, principally, 5. when it crystallizes between moist rocks.

If the average water content of clay, the most frequent kind of sedimentary rock, is estimated at 6,1% and that of the contact schists produced by its transvaporization at 3%\*, the maximum moisture resorption of a

\* These figures are supported by the following averages [8, 9, 10]:

	H <sub>2</sub> O <sup>+</sup>	H <sub>2</sub> O <sup>-</sup>
Blue mud (CLARKE).....	7,2	
Blue and green mud (STEIGER) .....	5,86	4,73
Red coastal mud (NIGGLI) .....	6,02	—
Red clay (CLARKE) .....	7,04	
Red clay (STEIGER) .....	5,93	3,28
Clayey Globigerina ooze (CLARKE) .....	7,90	
Molasse clays (SWITZERLAND, NIGGLI) .....	3,4—8,4	1,7—5,6
Mezozoic and Cenozoic clays and shales .....	3,45	2,11
Palaeozoic shales (CLARKE) .....	3,82	0,89
Lower Alsatian shale (ROSENBUSCH) .....	3,9	
Lower Alsatian Garbenschiefer (ROSENBUSCH).....	3,5	
Lower Alsatian andalusite-hornfels (ROSENBUSCH) .....	1,75	
Lower Alsatian tourmaline-hornfels (ROSENBUSCH) .....	0,64	
Albany (USA) shale, at 30 m from granite (ROSENBUSCH) .....	4,09	
Albany hornfels beside granite (ROSENBUSCH) .....	1,31	

square pyramid-like magmatic body will be 3,0%, supposing that the total breadth of the contact zone of the clay is equal to  $1/5$  of the breadth of the magma pyramid.\* One has to take into consideration, that the actual zone of water supply is wider than that of contact metamorphism, which is macroscopically observable (see below).

The amount of water and other moistures reserved in the interstices of sandy rocks can also be considerable. In his contribution to the discussion of this paper, Prof. A. FÖLDVÁRI pointed out that sandy country rocks, being good conductors, increase the possibility of transvaporization.

Geologically, the effect of transvaporization of pyroclastites on younger igneous eruptions is especially important. Pyroclastites are originally loose rocks *in situ*, accumulating considerable amount of water, which is released on magmatic effect.

The relatively most intensive effect of transvaporization is produced by coals, being the richest in volatiles. In the case of contact-metamorphism, coals alter easily — sometimes totally — into volatiles, and even at a relatively small increase in temperature they produce a large amount of it, namely, besides water, principally carbon dioxide. A similar effect can be observed in other rocks, containing carbonaceous matter, e. g. in bituminous limestones, black shales, etc.

Other, p. e. older igneous rocks may also produce transvaporization if their water content is sufficient. Some igneous rocks of higher water content have just been produced by transvaporization (see Chapter III); the effect of transvaporization exerted by such rocks on the subsequently intruded magma may be called secondary transvaporization.

On the effect of magma, a certain part of the volatiles penetrates through the country rock surrounding the magmatic mass, and through the fissures, even to the atmospheric surface. However, the percentage of this outwards

\* Andesite of average composition changes in case of resorption of 3% additional water as follows (initial weight percentages are andesite averages of DALY).

	Original		After resorption of 3% water	
	Weight %	Mol %	Weight %	Mol %
SiO <sub>2</sub> .....	59,6	63,9	57,8	56,8
TiO <sub>2</sub> .....	0,8	0,6	0,8	0,6
Al <sub>2</sub> O <sub>3</sub> .....	17,3	11,0	16,8	10,1
Fe <sub>2</sub> O <sub>3</sub> .....	3,3	1,3	3,2	1,2
FeO .....	3,1	2,6	3,0	2,4
MnO .....	0,2	—	0,2	—
MgO .....	2,8	4,5	2,7	4,1
CaO .....	5,8	6,4	5,6	5,9
Na <sub>2</sub> O .....	3,6	3,9	3,5	3,6
K <sub>2</sub> O .....	2,0	1,3	1,0	1,2
H <sub>2</sub> O .....	1,3	4,5	4,3	14,2
P <sub>2</sub> O <sub>5</sub> .....	0,3	—	0,3	—

Thus the significance of resorption of 3% water may be valued by the fact that it represents 14,2 mol%.



escaping volatiles is mostly small, as overlaying impermeable rocks affect volatiles as a trap (here using this petroleum geology term after A. FÖLDVÁRI). Obviously, such are argillaceous rocks. The escape of vapour cannot easily take place through the rock interstices of loose sediments filled with water. Moreover, the interstices and fissures of the country rock are filled up and soon closed, on the effect of volatiles by newly formed minerals. Consequently, the trap-effect quite generally appears.

The migration of high-pressure water into the magma is considerably facilitated by the decrease in water viscosity taking place at increase of temperature (E. NEMETZ). The decrease in water viscosity being quite considerable, even at a small difference in temperature, this factor considerably promotes the flow of water towards higher-temperature magma, even by a small increase in temperature, i. e. at a greater distance from the magmatic body. Thus a broad zone of country rocks, showing no other proper contact effect, yields water for the process of transvaporization.

Thus the water-resorbing effect of the magma, produced by the formation of the pressure slope, acts upon the whole environment, not only laterally and downwards but also upwards, within the zone of the trap-effect.

Transvaporization has a wide and intensive effect on magmatic processes and gives in many respects a completely new aspect of our concept about magmatism and contact-metamorphism. Some of these effects are treated in the following two chapters.

Obviously, one has to take also some related factors into consideration, e. g. the effect of constituents dissolved from country rock, the heat content of the magmatic mass, the heat conductivity of the country rocks, the depth of intrusion, etc. Considering the phenomenon of transvaporization, a comparative study of country rock will be indispensable, for the petrology of igneous rocks.

## II. Considerations concerning the system of igneous rocks

The above-mentioned phenomena of interaction of magma and water concern some problems of rock classification too. The system of magmatic rocks was hitherto based on the assumption of its own juvenile endogenous water content. Such originally mostly small amount of profound water can be accumulated mostly only after the main crystallization to such a degree that it could take an important part in the process of crystallization. This conception is reflected in the current classification of magmatic rocks by temperature, distinguishing liquid-magmatic, pegmatitic, pneumatolytic, and hydrothermal phases.

However, according to the foregoing chapter, water of transvaporizational origin can often play an important role in the crystallization of intruded

magma from the very beginning of the process. Consequently, many rocks exist which cannot be graded among the above-mentioned four categories of magmatic rocks. Because of an early abundance of transvaporizational water, these rocks are characterized by a considerable extension in the range of crystallization temperature. The crystallization of these rocks is not completed at liquid-magmatic temperature but it goes on in the pegmatitic, pneumatolytic and, even often in the hydrothermal phase. We propose to denominate *hemiorthomagmatites* those rocks, the crystallization of which takes place from liquid-magmatic to pneumatolytic temperature, and *hypomagmatites* those, the crystallization of which goes on from liquid-magmatic to hydrothermal temperature.

The characteristics of hypomagmatites in many respects are similar to those of rocks decomposed by subsequent hydrothermal alteration. Accordingly, one has to distinguish from hypomagmatites those rocks, the crystallization of which was completed at liquid-magmatic temperature, and which, as common orthomagmatites, were later hydric or hydrothermally altered or disaggregated. We propose the term "*metamagmatite*" for these rocks, and especially the term "*endometamagmatite*", in the case of hydrothermal alteration taking place in the earth's crust — mainly along fissures — and the term "*exometamagmatite*" in case of rocks disaggregated on the surface, dry or covered by water. Naturally, these denominations can only be applied to altered or disaggregated rocks the dominant characteristics of which are still undoubtedly igneous. Thus — using the principal tripartite classification of rocks into igneous, metamorphic, and sedimentary rocks — these are still to be classed among igneous rocks. Therefore, this classification does not concern e. g. the different sorts of soils formed during weathering, i. e. the products of the horizons *A* and *B* used in pedology. However, according to the proposed nomenclature, the rocks of horizon *C* represent exometamagmatites.

While the formation of hypomagmatite represents a real magmatic process, the formation of metamagmatites belongs to the range of epigenesis.

The term metamagmatite cannot be confounded with orthometamorphites and parametamorphites, or more accurately with plutometamorphites, volcanometamorphites and sedimento-metamorphites. The latter are easily distinguishable from the two groups of metamagmatites: *metaplutonites* and *metavolcanites*.

By transvaporizational hypomagmatism, the concept and geological importance of the so-called *endogenous contact* processes are considerably widened. The data enumerated in the following chapter prove that the role of the so-called endogenous contact rocks is considerable in the earth's crust. They are, however, not real "contact metamorphic" rocks, not being metamorphic products of solid rocks, but represent igneous rocks issued of transvaporized magma. Because of the overwhelming majority of hypomagmatic

origin, one has to class them mostly in the new, independent igneous rock group, called hypomagmatite.

However, hemiorthomagmatic or hypomagmatic rocks, and the effect of transvaporization, are *not always* observable in the rock veins and chimneys breaking through the originally moist rocks. Namely, if a large amount of magma migrates through such channels, the effect of transvaporization of the water-containing country rock is exhausted by the magmatic mass at first passing through these rocks. A transvaporization of the subsequent vein-filling magma by the country rock already dried and contact-metamorphosed is not possible any more. On this basis, the principal chimneys and dikes are probably distinguishable from ephemeral veins and secondary chimneys.

As moist country rock is much more frequent in the subvolcanic than in the plutonic conditions, hypovolcanites are more frequent than hypoplutonites.

The above-exposed classification of magmatites, expressed by approximate temperatures of crystallization, can be summarized as follows :

1200 to 700°C=orthomagmatite

700 to 500°C=pegmatite

550 to 400°C=pneumatolyte

400 to 50°C=hydrothermalite

1200 to 400°C=hemiorthomagmatite

1200 to 50°C= hypomagmatite

1200 to 700 and 400 to 50°C=endometamagmatite

1200 to 700 and lower than 50°C=exometamagmatite

It is unnecessary here to touch upon the well-elaborated system of orthomagmatites. In the present paper we also do not treat the problem of hemiorthomagmatites, nor that of hypoplutonites and metaplutonites.

First of all, we here treat hypovolcanites and metavolcanites, the petrological relations of which we have already thoroughly studied.

### III. Hypovolcanites so far examined

The most important among transvaporizing volatiles of exogenous origin, migrating into the magma, is water. On the *effect of water*, various kinds of rocks are formed, depending on temperature, pressure, pH and oxidation-reduction values of the environment. Let us see first some general trends of these processes.

If the overwhelming majority of water penetrates into the magma in the initial phase of solidification and its effect is mainly exerted at relatively high temperature, volcanic rocks with *biotite* and *epidote* (zoisite) — belonging for the most part to hemiorthomagmatites — can be produced at relatively low pH. This neutral or weakly acid reaction is probably due to the initial high concentration of water vapour, alkalis dissolved from the magma



or from the feldspars of the crystallizing rock not being sufficient to produce higher pH values of such a greater quantity of suddenly escaped transvaporizational water.\* (See No. 7. p. 211—212)

If moisture is gradually resorbed by the magma during the course of the long interval of crystallization, it exerts a considerable effect, even at hydrothermal temperature. In this case e. g. chlorite and serpentine-bearing rocks: *chlorovolcanites* e. g. hypovolcanitic propylite (see below) are formed in a more or less neutral medium. (See No. 3, 8a and 9.)

If the effect of moisture is mainly exerted in the advanced phase of the crystallization, feldspars are decomposed in the pneumatolytic phase, whereby the solution may become alkaline on the effect of the alkalis of the feldspar, especially in the case of lower water quantities. From this solution, zeolites can be produced at a lower temperature, by the hydration of the decomposed feldspars. A type of *analcite-basalt* is one of the principal products of such a crystallization. (See Nos. 1 and 4)

Consequently it may be assumed that, by decreasing temperature, decomposition gradually advances from dark silicates to feldspars. Dark silicates and many other iron minerals are not stable at higher temperatures, in the presence of water, in acid reducing medium; the solution so produced crystallizes but at a lower temperature, as biotite, chlorite, etc.

Among volatiles of exogenous origin, migrating into the magma, *carbon dioxide* can also play an important part, especially if the magma penetrates into sedimentary rocks containing organic matter. In the presence of water, the carbonate minerals of the country rock can be dissolved too. Thus in the igneous rock, carbonates are formed on the effect of carbon dioxide immigrating into the magma. In this way siderite and sphaerosiderite are produced from the alteration of iron silicates, and calcite from calcium silicates. The term *carbovolcanite* (e. g. carboandesite, carbodolerite, etc.) may be employed for such rocks. (See Nos. 3, 5, 7, etc.)

In the surrounding sedimentary rocks containing organic substances, the magmatic heat effect may also release *sulfur*, which produces pyrite, with the iron of decomposed iron minerals in the igneous body. We call *sulfovolcanites* the rocks so formed. (See No. 5).

Observations made on contact rocks at Nagybátony show that carbovolcanites are produced rather in the high-temperature parts of the coal contact, while sulfovolcanites in the low-temperature parts of the contact nearer to the sedimentary rocks. At the coldest margin, a thin montmorillonitic hydrovolcanite zone is also present. These relations are shown by the analytical measurements of our pupil T. PÓKA, summarized in Fig. 5.

\* A special study on country rocks is needed to elucidate whether the hydrothermal feldspar-muscovite zoisite parageneses of abyssal rocks, pointed out by ERDMANNSDÖRFFER [57] are partly the products of transvaporization or not.



The most important, so far recognized, types of hypovolcanites will be described in the order of increasing water content and rock acidity :

A) *The lava flows on moist (sedimentary or other) rock.* This is principally important in case of basaltic magmas forming large lava covers. It is less significant in more acidic and viscous magmatic body of lower temperature, covering the substratum to a smaller extent and thus permitting a more intense lateral escape of vapour.

1. If basaltic lava flows on a moist, e. g. argillaceous, rock, the high-pressure vapour produced by the effect of lava takes part particularly in the

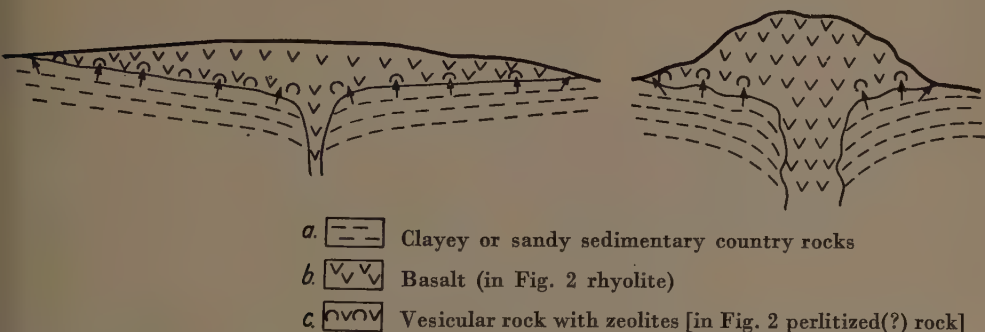


Fig. 1. Transvaporization of basic lava flow

Fig. 2. Transvaporization of acidic lava (plug dome)

last phase of the relatively rapid crystallization of the basic lava. Feldspars are decomposed at pneumatolytical temperature and the solution formed thus, later hydrothermally crystallizes at about 100° C, as zeolite. So *analcite-basalts* containing zeolite in their matrix, and basalts containing cavities with zeolitic mineral associations are formed. Occurrences of such rocks in the vicinity of Lake Balaton described by B. MAURITZ [12, 13], seem to be good examples for this process and were recently investigated by us, together with J. ERDÉLYI [14] (Fig. 2).

It follows from this genesis that zeolitic basalts are not formed on a substratum of moisture-free rocks. This is also observable in Mount Kabhegy of the Balaton-country and in the majority of the basalts of Nógrád, in the North of Hungary.

According to KLÜPFEL [15], the formation of zeolites requires higher pressure, therefore it chiefly characterizes the "intrusive basalts". However, as we have described, higher vapour pressure is also produced by lava flowing on moist rock, and zeolitic basalts are therefore present in lava flows too.

Some other ways of the formation of zeolite are below described.

2. In the case of more acidic magma, the effect of transvaporization of the sedimentary basement is generally less considerable, according to the above-mentioned principles. It is most likely that members of the *perlite-pitchstone* group (see No. 11, p. 214.) and, on the other hand, — in consequence or more intense leaching by the lateral escape of vapour — under such circumstances *leucovolcanites* and *hydrovolcanites* are formed too. (See chapter IV.) (Fig. 2).

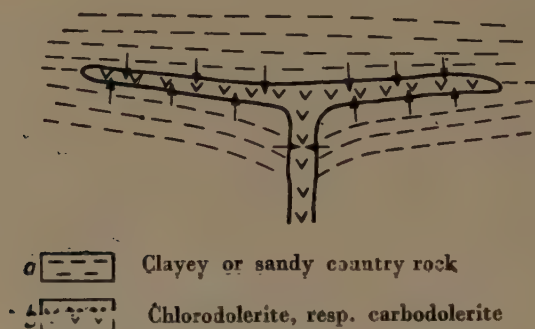


Fig. 3. Transvaporization of basic sill

B) *Subvolcanic magmatic mass is consolidated as intrusion in moist rocks*

3. Thin-liquid, basic magma consolidates as sill, between moist strata. The speed of cooling decreases in the presence of overlying rocks, consequently the rock thus formed is coarser-grained, doleritic. In accordance with slower crystallization, the moisture of transvaporization already affects the earlier products of crystallization. Depending on the composition of country-rock, chloritic dolerites (*chlorodolerites*) are formed or, in sedimentary rocks containing organic matter, *carbodolerites* often with siderite or sphaerosiderite (see Fig. 3).

One may range among chlorovolcanites and carbo(chloro)volcanites produced by transvaporization such rocks as *weilburgites* of the Lahn-Dill iron ore district, further the carbodolerites and weilburgite-like chlorodolerites found under 2000 m in the deep-boring near Szany (Little Hungarian Plain). In both cases, there also appear mixed igneous-sedimentary rocks (mictites), called "*Schalstein*", showing the marks of weak assimilation too. Considering the formation of more acid alkaline rocks in connection with the transvaporization of basic subalkaline rocks, described below (No. 4), it seems possible that the formation of the so-called *keratophyres* of the Lahn-Dill-Mulde containing chlorite, muscovite and carbonates represents carbohydrovolcanites [17] derived from doleritic magma by transvaporizational processes.

4. There is another type of sills of basic rocks, formed by transvaporization. This one may be called *zeolite sill type*, and it is characterized by its considerable thickness (for the most part 25 to 150 m), complex composition, and a concentric structure. The country rock on direct contact mainly consists of contactized sedimentary rock, which is followed inwards by a fine-grained basaltic margin, then by a zone of *analcite-dolerite*, or *teschenite* or *analcite*

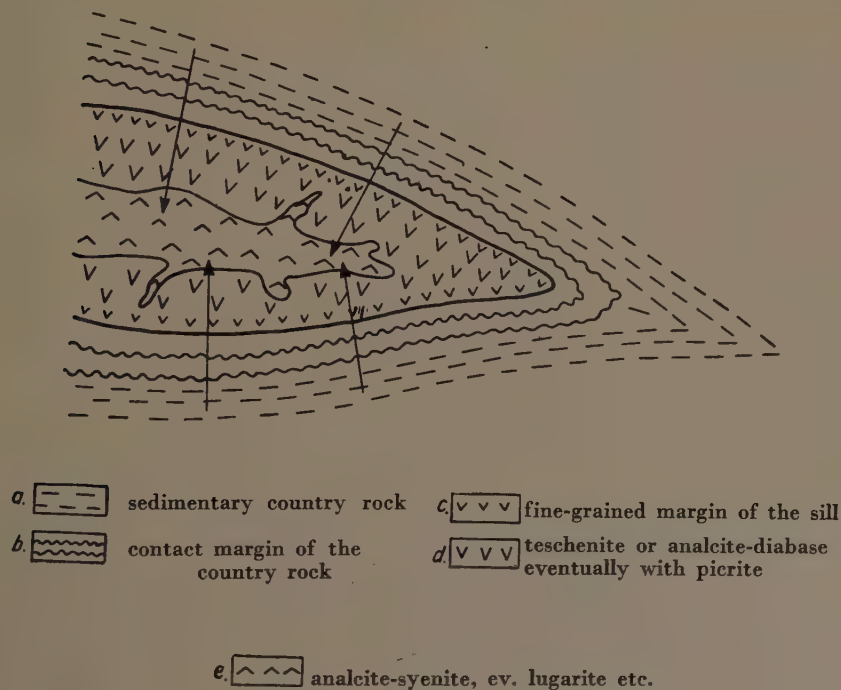


Fig. 4. Thick basic sill with a core of alkaline rock

olivine diabase (*crinanite*), and eventually also of *picrite*; the central part is mostly formed of an *analcite syenite*-core with or of veins of *alkaline pegmatite* and *analcite-aplite* (e. g. *lugarite*). Thus the crystallization of the basic sub-alkaline zone, is succeeded, in the centre by the formation of alkaline rocks. The two main types of these rocks are partly separated by a sharp border, and partly by gradual transition (Fig. 4).

The most characteristic examples of this type are described from Scotland and the Hebrides. The Lugar sill, the Howford Bridge sill and the adjacent ones of Ayrshire, described by TYRELL, those of Shiant Isles, described by WALKER, belong to this type. Similar magmatic bodies are known of Utah (GILLULY) and Corea. The peridotite sill of Kaersut (Greenland), traversed by alkaline pegmatite veins and nests, described by DRESCHER-KADEN is

closely related to this type too. The complex "pine-like" structures inwards becoming ultrabasic, described in the following passage, also show some transitions to this type [58—63].

The above-mentioned authors agreed on the high water content and ability to the particular differentiation of the parent magma of these sills. It has also been assumed that the magma of the basic rock at first erupted and it was followed, in the course of its solidification, by the alkaline-magmatic intrusion. The "auto-intrusion" theory of BOWEN has also been applied; according to this, the alkaline rock core and veins are produced from the residual alkaline magma pressed out of the interstices of the crystal lattice. The displacement of residual magma is attributed to a tectonical effect by BOWEN, to roof pressure by TYRELL, to the pressure of volatiles by BAYLEY. DRESCHER-KADEN derives the Kaersut alkali pegmatite from peridotite by the assumption that lateral secretion takes place after the solidification of the magma.

The problem of the particularly high water content of the magma of sills, however, has remained unsolved by this descriptions. Being sills no apices of the magma body, they are not suitable for the accumulation of volatiles. On the other hand, one could hardly imagine a consistent intrusion of both kinds of magma in the same sill, or even the cause for the continuous pressing of alkaline residual magma into the centre of such sills.

The formation of this type of sills becomes, however, plausible by the principle of transvaporization. All sills of this type have been solidified in a sedimentary country rock. The neighbouring moist sedimentary rock necessarily exerts an effect of transvaporization on the magma. This is proved directly by the contact metamorphism of the marginal zone of these rocks. Thus the crystallization, differentiation and other characteristics of these sills are fundamentally determined by transvaporization. At first such a characteristic is the extraordinarily high water content of their magma, which may not be the result of any unknown abyssal process, but it is of exogenous origin, deriving from the sedimentary country rock. The formation and separation of alkaline rocks from non-alkaline basic rocks in the centre of the sill necessarily results from the high-pressure transvaporization vapour too. Upon this effect the residual magma — becoming less viscous — is gradually pressed from the crystal mesh of the solidifying magma towards the interior of the sill. The amount of alkalis in the hydrated residual magma may be increased by the alkalis dissolved from the surrounding sediments. Thus there is segregated a particular analcite-syenite core or alkaline pegmatite veins in the interior of the subalkaline (ultra-)basic magma body.

The basic margin towards the interior sometimes becomes ultrabasic; this may also be a result of transvaporization, as will be shown, in connection with pine-like magmatic bodies described below (No. 6).

The question, however, may be raised why these zeolitic rocks are



sometimes formed in the transvaporized basic sills by a partial decomposition of the feldspars, whereas, at other times, chlorodoleritic rocks described in the foregoing passage are produced by a chloritic substitution of dark silicates. Probably this fact results from the differences in pH concentration of transvaporizational water. It is known that a high-alkaline medium is required for the formation of zeolites, while chlorites and sericite for the most part are produced in a neutral or a weakly acidic medium. In thin sills a given volume of magma has a comparatively large boundary surface, thus it gets a larger amount of transvaporizational water, than a thicker, more isometrical body. In the case of the thin sills the comparatively large amount of water remains roughly neutral, not being greatly changed by the alkalis dissolved from the magma or from their feldspars, respectively. Thus thin sills are more favourable for the formation of chloritized dolerites. On the contrary, in thick sills, the amount of transvaporizational water per unit volume of the larger magmatic mass will be smaller. This smaller amount of water may become more alkaline by the alkalis dissolved from the feldspars of the crystallizing magma, consequently, thick sills produce a medium suitable for zeolite formation. As a matter of fact, zeolite sills known up to the present are all of considerable thickness. Similarly, lava flows on moist sedimentary rocks getting only a small amount of water from the bottom of the lava flow, produce zeolitic basalts, thus proving it as alkaline medium.

5. Carbovolcanites and chlorovolcanites are not attached exclusively to doleritic-basaltic composition, nor to the sill. In the former passages it was pointed out that similar rocks may develop with much more acidic composition too. (Analcite-syenites, lugarites, alkali pegmatites, Lahn-Dill keratophyres.) Carbovolcanites and chlorovolcanites can, on the other hand, appear, also in magmatic dikes. *Carbovolcanites* are especially produced on contact of magma with coal, on the effect of carbon dioxide and other high volatiles derived from coal. We have to consider, as such a *carbotrachydolerite*, the endogenous contact product of the trachydolerite veins of Komló, Hungary, occurring beside bituminous coal, described by Széky-Fux [35], and as *carboandesite*, *sulfoandesite* and *hydroandesite* the contact rocks of lignite in the environments of Nagybátony, Hungary, recently studied by T. Póka (Fig. 5).

6. If the basic magma penetrates to greater depths — particularly in a folded orogenic territory, — into argillaceous rocks viz. shales, it can produce a complex, "laccolith-like" magmatic body branching out in several horizons forming a pine-like structure. In this case, the moisture content deriving from the sediments may almost exert its effect according to the slow cooling of the magma during the whole process of crystallization and, thereby, the magma becomes greatly differentiated. As iron and titaniferous minerals are not produced in the presence of moisture at high temperatures, feldspars are crystallized first, especially on the more rapidly cooling margins of the magma

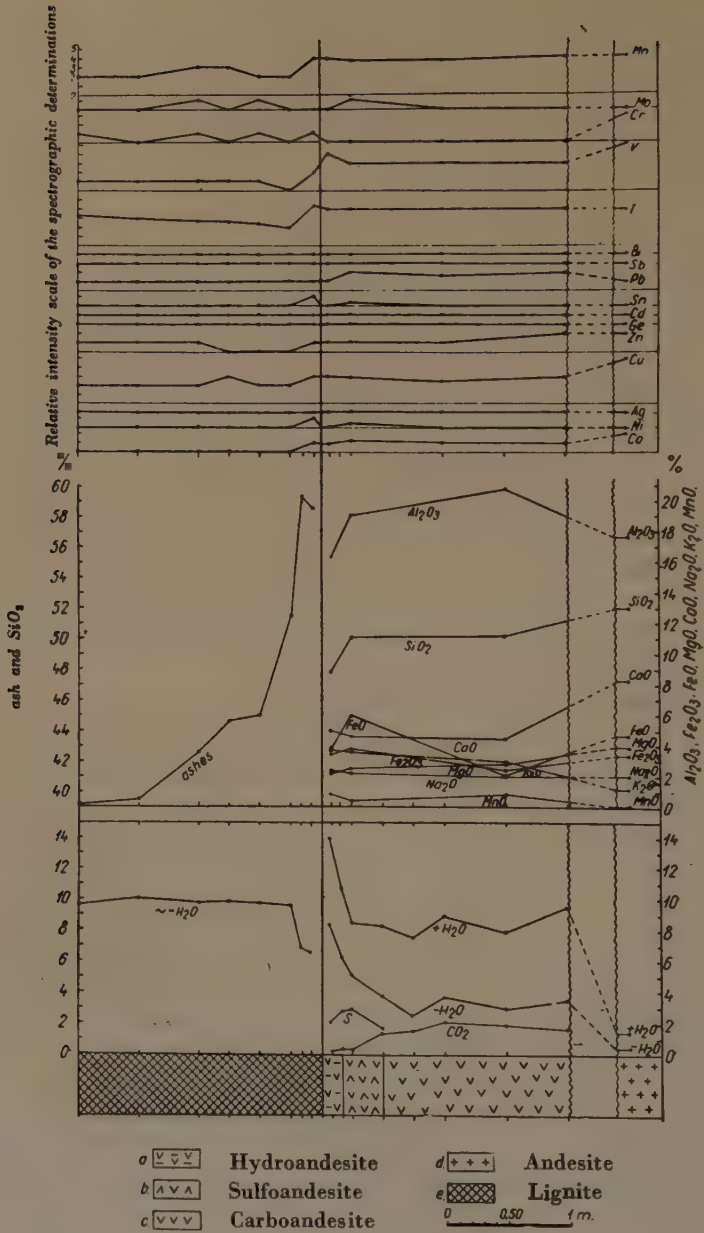


Fig. 5. Contact of a tertiary lignitic coal with andesite dyke at Nagybatony, Hungary  
Chemical analysis by T. PÓKA ; spectrographic determination by I. KUBOVICS

body. Consequently, the rocks formed on the margins are richer in feldspar, and more acidic. The iron and titanium compounds, the potential of which decreases on the effect of the hydroxyl content, pressed by the vapours of transvaporization into the warmer interior of the igneous body crystallize later, after dehydration. They produce ultrabasic rocks of a higher Fe—Ti concentration. Such bodies together with many other kinds of peridotitic rocks (*wehrlite*, *peridotites* rich in titanium ores, *hornblendites*) of the Bükk Mountains, are described in detail by SZENTPÉTERY [36] and LENGYEL [37]

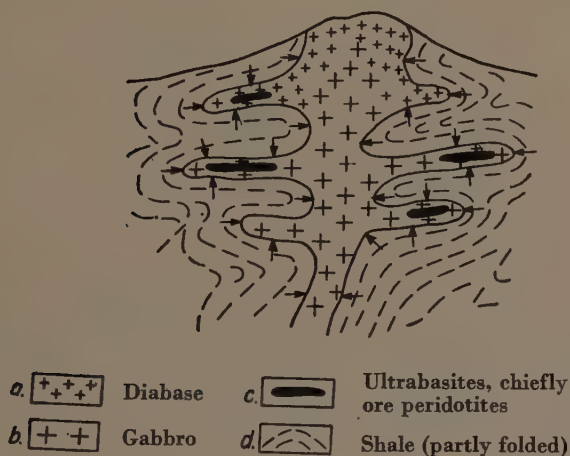


Fig. 6. (Ultra-)basic "pine-structure" (partly according to E. LENGYEL)

(see Fig. 6). LENGYEL pointed out that titaniferous ultrabasites are also known in other shaly environments. However, shale country rock is not to be expected always in the environment of these rocks, for the very reason that shale can subsequently be transformed into crystalline schist. On the other hand, other moist rock than clay and shale may exert transvaporization too.

Thus, the order of crystallization of the basic magmas may considerably change and even become nearly opposite, this fact in some measure elucidates the formation of *ophitic texture* of diabasic rocks.

7. If a neutral, i. e. more viscous and therefore more slowly moving and wider magma mass penetrates — generally near the surface — into a complex of moist (mostly clayey) rocks, a vapour-cap is produced over the magmatic chimney between the magma mass and the moist country rock. On route laterally cut by the vapour-cap, the magma penetrates between the strata and, bending up the overlying rocks, forms the laccolith (Fig. 7). The vertical advancement of the igneous body, thus widened like a nail head by the vapour

cap, is hampered by the backward pressure of the overlying strata. This mechanism — the details of which are not mentioned here — sufficiently elucidates the widely discussed, unsolved problem of the formation of laccoliths and is in accordance with a still unnoticed phenomenon, namely, that the rocks surrounding laccoliths are chiefly of sedimentary, mostly clayey origin, originally rich in volatiles. The details of this question are expounded in a paper on Mount Csódi (Dunabogdány), written by the author and his collaborators I. KUBOVICS, L. PESTI, and Cs. RAVASZ [16].

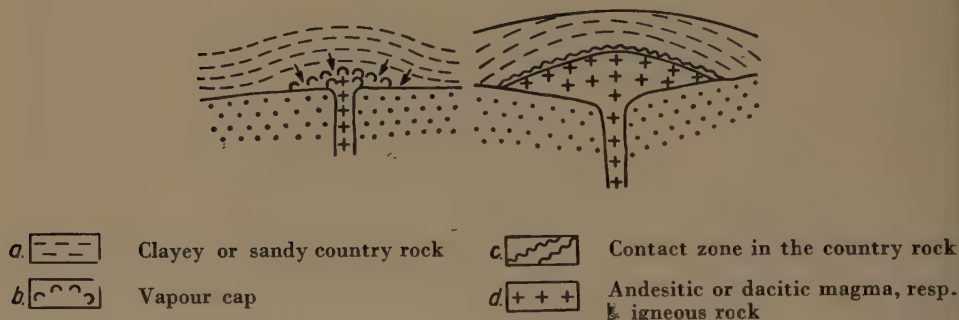


Fig. 7. The beginning and the end stage of the formation of a laccolith

The high-pressure vapour-cap produced at the beginning of the process, principally effects the initial phase of the consolidation of laccolith. After the development of the vapour-cap, no considerable moisture can subsequently be released from the country rock, at lower temperature, consequently crystallization is mostly completed in the hemiorthomagmatic state. The vapour-cap, with silicic acid and alkalis leached from the clay, may produce biotite and, with the calcium of feldspar, on the margin of the magmatic body, zoisite. The *biotitic-zoisitic-marginal* andesite or dacite thus formed is rather an hemiorthomagmatite. On the contrary, the main central part of such laccoliths is mostly characterized by nearly normal andesitic, dacitic or similar rocks.

8a. If a neutral and more viscous magma penetrating into moist country rocks is blocked at a greater depth, there is produced, in accordance with the higher pressure of this depth, a supercritical fluid solution instead of a vapour-cap. The magma forms a less regular subvolcanic body, namely chonolith. In this case the fluid solution is not so rapidly pressed into the magmatic body as the high-pressure vapour-cap, but diffuses more slowly in it, consequently the solution effects the crystallization process during a longer period, at lower temperatures too: there are formed chlorite, eventually serpentine, epidote, sericite and carbonates. *Hypovolcanitic propylite* bodies



forming independent subvolcanic masses, generally with a broad contact zone, in preponderantly clayey country rock, are formed in this way (Fig. 8).

Hypovolcanitic propylitization roughly corresponds to the process of propylitization described by RICHTHOFEN [19], PÁLFY [20], BÜRG [21], SCHNEIDERHÖHN [22]. However, it is not produced by autohydration caused by the own endogenous volatiles of the magma (autometamorphism) but by volatiles of the country rocks penetrating into the magma by transvaporization.

However, there is another way of propylitization, namely the metavolcanitic propylitization, described in the following chapter (p. 218.)







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| a |  | Clayey, sandy and pyroclastic country rock | c |  | Propylite |
| b |  | Contact zone in the country rock           | d |  | Andesite  |

Fig. 8. Hypovolcanitic propylite-body (from a section of Visk described in [18]).

It may be assumed that the border between the formation of laccolith and that of propylitic chonolith is to be drawn at a depth of more than 800 m, the critical pressure of water (218,5 atmospheres) corresponding to about this depth. The water being namely confined in the pores of the rock, the pressure is there less than the rock-pressure.

8b. The intrusion of acidic magma into moist rocks probably produces the members of the perlite-pitchstone group (see No. 11) or, at a greater depth, muscovitic-chloritic hypovolcanites similar to the above-mentioned keratophyres of the Lahn-district. This is probably also valid for submarine eruptions at greater depths.

C) *The lava flows into water.* The effect of transvaporization is the highest in such cases.

9. If the basic lava erupts in abyssal sea-floor, e. g. in the geosynclinal phase representing initial volcanism, there is no formation of vapour, in accordance to the high pressure of the deep ocean. Chlorite is produced from or instead of augite, amphibole, biotite. Instead of basic plagioclase, albite is partly produced on the effect of the sodium-rich sea-water, and, besides this,

epidote and perhaps calcite. This is the process for the formation of *spilites* and *ophiolites* recently studied by AMSTUTZ [23].

10. If the basic magma forms submarine eruption in a not very deep sea, besides lava rock it probably produces some pyroclastites, due to the explosion by the intensive vapour development. Probably, the formation of *pillow lava* belongs partly to this process too. On the other hand, pillow lava with a clayey matrix — called globular basalt by KLÜPFEL — seems to correspond to a volcanite of globular (spherical) joint, which we shall treat in Chapter VI. (pp. 227—228).

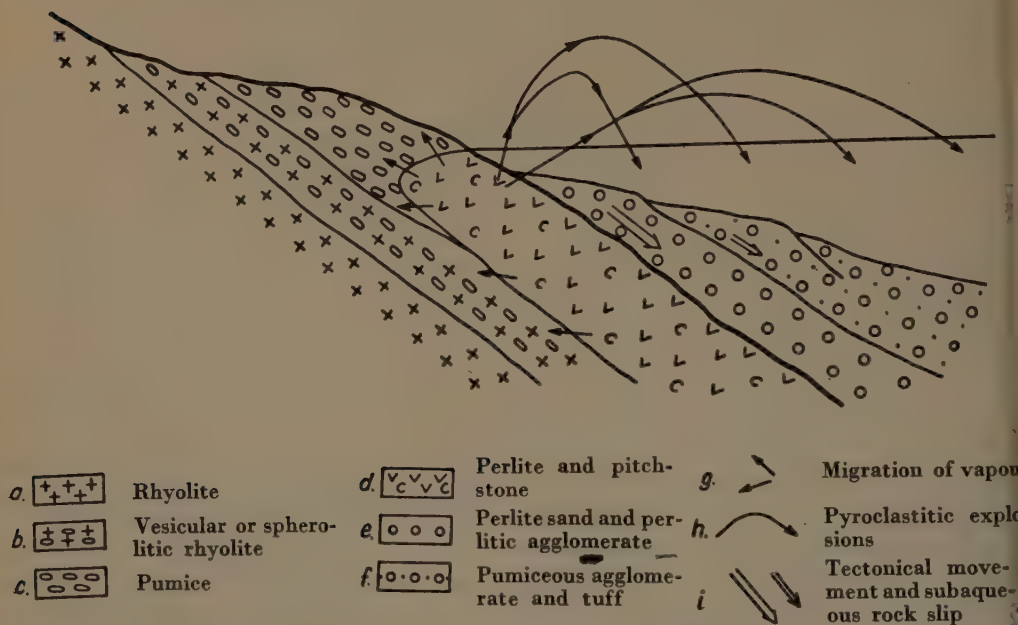


Fig. 9. Relation among rhyolite, perlite, pitchstone, pumice and their pyroclastites

(Migration of vapors from seawater into perlite-pitchstone is not represented.)

11. Acidic lava flowing into shallow water produces vapour of high pressure, stirring up the lava and even pressed into it. At the same time the viscosity and melting point of the lava decreases, the vapour also penetrates in it by diffusion and is dispersed. In less turbulent phases of the magma-water contact this process is also facilitated by the Leidenfrost-phenomenon. In this way *perlite* and *pitchstone*, often alternating in a banded form, are produced on the effect of a syneresis-like separation of two immiscible phases of different water contents. In those parts where the lava is richest in vapour, e. g. at the top of the lava-body, containing ascendant vapour, the lava blows up (Fig. 9) and alters into *pumice*. From the perlitic, pitchstone-bearing and

pumiceous zone, vapour penetrates towards the interior of the lava mass too and there produces a *scoriaceous* and *spherulitic* rhyolite type. The formation of vapour accompanied by explosions also produce pyroclastites, forming *perlitic rhyolite tuff (agglomerates)*, and further *pumiceous tuff (agglomerates)*, chiefly on the external side of the perlitic lava front (Fig. 9). On the steep side of the lava flow, a zone of subaqueous slidings in loose deposits develops too. Perlite sand, mostly appearing on the border between the solid rhyolite-perlite complex and the loose pyroclastite series, is mostly suitable for structural movements; such effects may play a considerable role in the formation of perlite sand. This possibility is also confirmed by the observation of E. SCHERF and E. KUBOVICS. Naturally, tuffs and pyroclastic agglomerates are formed in many other ways too.

12. Neutral lava flowing into water is probably accompanied by perlitization, and perhaps bentonitization and, at greater depths, by propylitization. CHESTERMAN [24] has recently pointed out the existence of perlitic andesites and dacites. Montmorillonitization of andesite lava flows in shallow paludal water was observed by the author in the Szinyák Mountains, near Užgorod.

While the initial submarine eruption of basaltic lava and the subaquatic eruption of rhyolitic lava belong to the normal course of geological evolution, neutral andesitic eruption does not have such a close causal relation to the subaquatic eruptions. Therefore, subaquatic, hypovolcanitic formation of andesitic lava is relatively scarcer.

Summing up the most important hypovolcanites, we may establish a certain transition from greater depths of intrusion towards the smaller ones, and from basic magmas towards acidic magmas. I. e. the degree of crystallinity is decreasing more or less by the decreasing depth of crystallization, further by increasing rock acidity and by the increasing water content of the rock. This is partly obvious, for it is well-known that the degree of crystallinity is higher in the depth, cooling slowly, and in less viscous basic lavas. However, supposing an endogenous magmatic origin of water, it is hardly understandable why hypovolcanites of high water content show a low degree of crystallinity, whereas volatiles should rather increase the degree of crystallinity. On the contrary, if water is derived from an exogenous source, the contradiction disappears, for crystallinity is decreased on the cooling effect of exogenous water.

This description is naturally far from establishing any complete system. Further investigations will evidently prove a much greater variability of hypovolcanites. Different relations to metavolcanites may be pointed out too, according to the connection of fissuring formation with the crystallization of hypovolcanites. A preliminary synopsis is however, given in Tab. I and fig. 3, p. 224.

#### IV. Metamagmatites

According to the nomenclature of Chapter II, the formation of endo-metamagmatites is due to the decomposition in the crust of orthomagmatic rocks, while exometamagmatites are produced by surface weathering. The former process becomes more intensive, and takes the character of leaching along fissures, dikes, and zones of structural movements. The increase in leaching is accompanied by the dissolution of silicon and — in order of intensity — starting from feldspars, it produces the series of clay and other Al-minerals: feldspar → illite → montmorillonite → kaolinite → bauxite minerals. The solutions, basic at lower water concentration (formation of montmorillonite), become later — in consequence of the leaching out of alkalis by increasing water concentration — gradually more acidic (formation out of kaolinite). Further on, oxidizing effects becoming prevalent, an increasing formation of bauxite minerals may take place.

Thus hypovolcanites and metavolcanites are principally often different in chemical constitution. Hypovolcanites are characterized by the *admixture of exogenous substances*, i. e. by the infiltration of transvaporizing volatiles, while in the case of metavolcanites selective *exsolution of substances* by subsequent leaching is preponderant. Therefore, in the metavolcanites the original proportions of magmatic constituents may often become considerably changed, while these proportions remain nearly unchanged in hypovolcanites.

##### A. Exometavolcanites

Before attaining the soil phase — besides the common C-horizon rocks — some peculiar exometavolcanites are also formed by particular surface effects.

1. The formation of exometavolcanite in *continental environment*, in a highly oxidizing medium, e. g. in or near volcanic craters, results in an oxidic transformation of minerals containing multivalent iron, by which, a kind of *oxy-volcanite* with red hematite is produced. We observed Miocene occurrences of oxyandesites e. g. in the Mátra, Börzsöny and Dunazug Mountains in Hungary, while recent formations of the same have been observed, around the fumaroles of the Parícutín, e. g. by G. PANTÓ [25]. Superheated water vapour affects evidently often this process.

Presumably, the formation of such rocks may also be possible at some depth under the surface around the fumarolic craters. Occurrences at the top of some crater-like hills in the Börzsöny mountains observed by M. CSÉSZKÓ seem to belong to this class of rocks.

2. The submarine halmyrolitic decomposition of volcanites in aerated water, may similarly produce *oxy-volcanites* which extend on the effect of infiltrated water. We have pointed out such a case, with V. SZÉKY-FUX, K. BALOGH and M. HERRMANN, in connection with the andesite of Komló [26]. In contrast to the foregoing type of oxy-volcanites, this type seems to be rather a limonitic rock (limonitic oxyandesite).



The formation of oxy-volcanites becomes more frequent with the increasing geological age. Presumably, *oxy-porphyrites* are therefore not rare either.

3. More intensive subaqueous decomposition, and perhaps also surface weathering, produce pale whitish *leucovolcanites*, principally by leaching a certain part of the iron compounds being the most mobile, because of the presence of a multivalent element [26]. Most frequently we found leucoande sites. They are sometimes more „acid” while oxyandesites are sometimes more „basic” than fresh andesites. Some leucovolcanites may also be of transva-porizational, hypovolcanitic origin.

4. By a more prolonged and more intensive leaching, the removal of silicic acid begins, forming montmorillonite and thus a considerable part of *halmyrolitic bentonites* from andesitic, as well as from dacitic and rhyolitic rocks are formed.

### B) *Endometavolcanites*

Endometavolcanites are partly formed along fissures conducting solutions — frequently in connection with the formation of ore veins — and, on the other hand, along structural crushed zones.

We treat ore veins and crushed zones, as two extremes, though in reality a gradual transition exists between them and they generally appear together. At the broadening of structural zones, endometavolcanites may considerably develop, forming wide zones of such rocks.

a) Profound fissures of ore veins during the course of geological ages obviously are not uniformly open, but they become narrower or even closed, partly at higher, partly at deeper levels. If the fissure is closed from above, the vein will be affected by ascending solutions and vapours. On the contrary, when it is closed in the depth, the effect of descending solutions will be predominant (Fig. 10). Thus, ascendant and descendant effects alternate in the ore veins.

The formation of the endometavolcanites shows certain graduation. In the following points the new rock types are arranged according to the increasing intensity of rock-alteration.

5. Minimum moisture effect only results in a superficial decomposition of minerals containing multivalent iron. E. g. in such a way, the small magnetites of the matrix of andesites disaggregate into fine-grained, magnetite-like soot and the rock darkens. At the same time, a fine-grained magnetitic margin is also formed around coloured silicates. Consequently, this phenomenon is very similar to the so-called opacitization taking place in connection with magmatic resorption, this phase is, therefore, called *metavolcanitic opacitization*.

6. In the following phase, the moisture begins to dissolve alkalis from silicates. In the alkaline solution thereby produced, even without any particular increase in oxidation-reduction potential, iron minerals are partly transformed into minerals containing iron of higher valency. Obviously, this sort

of oxidation can be intensified near the surface, by the increase in oxidation-reduction potential. The red or brownish oxyvolcanites produced in this way, by limonitization or by formation of hydrohematite, are called — in order to distinguish them from the above-mentioned similar exometavolcanitic rocks — *endooxyvolcanites*.

7. If the degree of leaching is sufficient for removing a certain part of the alkalis, the solution becomes neutral or even acidic. In such a medium iron silicates alter into chlorite, even also into epidote, i. e. the rock is propylitized. This type of rock may be called *metavolcanitic propylite* (chlorovolcanite phase). This kind of propylite — contrary to the hypovolcanitic propylite described in the foregoing chapter — does not form independent subvolcanic masses but

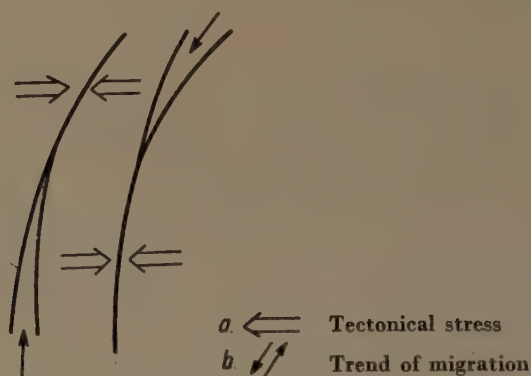


Fig. 10. Closing of fissures and trend of migration

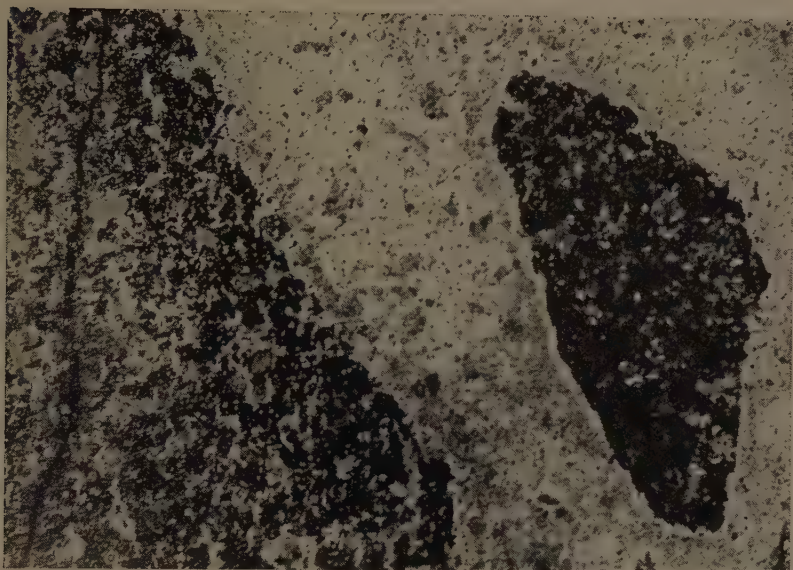
Left: the ascending, right: the descending stage in the fissure

it appears along dikes and fissured zones, as more or less narrow strips, often without sharp borders. J. SZABÓ [27], later ROSENBUSCH [10], H. BÖCKH [28], NAKOVNIK [29], BÁNYAI [30] and J. TREIBER [30] investigated and described this kind of the propylites, as generally characteristic for propylitization. While hypovolcanitic propylite for the most part appears between moist sediments and is surrounded by a considerable contact zone (e. g. in the Transsylvanian Erzgebirge and Gutin Mountains, see [53]), metavolcanitic propylite is often to be found in metamorphic areas (see e. g. [54, 55]). Propylites are mostly connected with *carbovolcanites*.

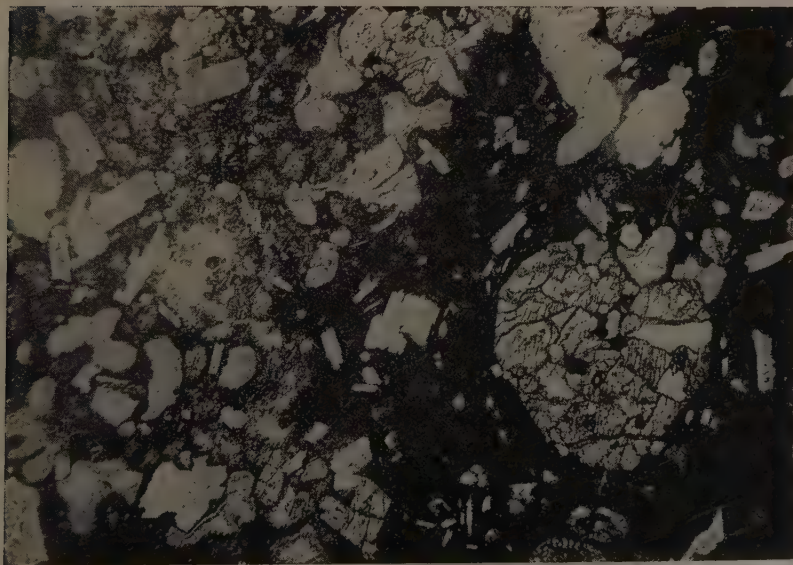
The long discussion on propylitization can be solved by distinguishing these two types of propylite.

8. Sometimes a partial dissolution of iron compounds also begins before the oxy-volcanitic and chlorovolcanitic phases, whereby pale, clear leucovolcanites are formed which are called — in order to distinguish them from the above-mentioned exometamagmatic rocks — *endoleucovolcanites*.

*Plate I*



a) Andesite-pseudoagglomerate with large opacitic andesite pseudog gravel, surrounded by thin leucoandesite margin, in hydroandesitic pseudo-matrix (actual size)



b) Opatitic augite-hypersthene andesite and its hypersthene leucoandesite margin (magnification 60 $\times$ )



In such a case, the less stable augite may be first decomposed among the pyroxenes, while hypersthene remains. In this way a primary augite-hypersthene andesite alters into hypersthene andesite as shown in Plate I, b. In other respects this sort of *hypersthene andesite* is like a fresh undecomposed rock. Thus several kinds of volcanites differing in coloured silicates, are not exclusively formed by endogenous magmatic differentiation, but sometimes they are exogenous products of a partial decomposition or due to different degrees of crystallinity.

9. Now the process of leaching gradually passes by exsolution of silicon, into different kinds of *hydrovolcanites* with clay minerals.

The first member of the hydrovolcanites is *hydrothermal bentonite* still formed in an alkaline medium. Such rocks from the Tokaj-Mountains and Komlóska described by V. SZÉKY-FUX [32] and K. KULCSÁR [33] may be ranged among the first group of hydrovolcanites. V. SZÉKY-FUX pointed out that hydrothermal bentonite could be formed not only from rhyolite but from andesite too. Important data on such rocks have been published by A. FÖLDVÁRI too [34].

10. In case of more intensive leaching, the total escape of alkalis produces a distinctly acidic environment where kaolin is formed by further exsolution of silicon. The kaolinization, well-known in many places along ore veins, belongs to the range of these *endometavolcanitic kaolinites* (see e. g. the descriptions by M. PÁLFI, [20]).

b) By the crushing effect which takes place in structural zones, irregular *lava breccia* is formed. Volcanite with a globular joint (see p. 227 and fig. 17) is regionally produced by the development of a more regular system of lithoclasts representing three main directions, which are perpendicular to each other. From such rocks — as well as from true agglomerates — the above-mentioned phases of opacitic volcanite, leucovolcanite, oxy-volcanite, chlorovolcanite, carbo-volcanite, montmorillonitic and kaolinitic hydrovolcanite can develop on the increasing effect of solutions.

11. In structural zones the described kinds Nos. 5—10 of metavolcanites are often observable *beside each other* within the same mass. They are formed by the chemical changes produced by the solutions migrating along the joints and irregular cracks. In such cases, larger parts of the original rock are still fresh or darkened into the opacite stage, while the smaller ones are altered into oxy-volcanite, or chlorovolcanite carbovolcanite, and leucovolcanite stages, the smallest into the hydrovolcanitic stage. In this way, the primary lava rock (and even original pyroclastic agglomerates too) may alter, by the decrease of grain size of the apparent rock fragments into *pseudoagglomerate*. This at first is like a coarse-grained *monomikt* pyroclastic agglomerate, later like a typical *polymikt* agglomerate (Plate I. a and Fig. 11). Its resemblance to true agglomerates is increased by the delimitation of the parts being in



different stages of alteration by sharp borders according to their distinct qualitative leaps by a series of alternations, and can even be separated by reaction rims, appearing particularly in the initial phases. Oxydated and reduced phases show syneresis-like separation.

However this borders are not equally sharp on all sides, they even vanish completely. The successive stages of the alteration are thus spreading in the rock as blots in the blotting paper.

Therefore, pseudoagglomerates even in fragments torn out of their geological connections, are distinguishable from true agglomerates. Pseudoagglomerates are often characterized 1. by a blot- or finger-like ramification of the grain borders, 2. by the prolongation of the direction of the hypoparallely oriented feldspar microlites (flow-texture) through different grains, and 3. by partly fractured plain, partly globular, convex borders of the fresh parts of the rock protruding from the decomposed rock matter showing different stages of alteration (Fig. 17, p. 229.)

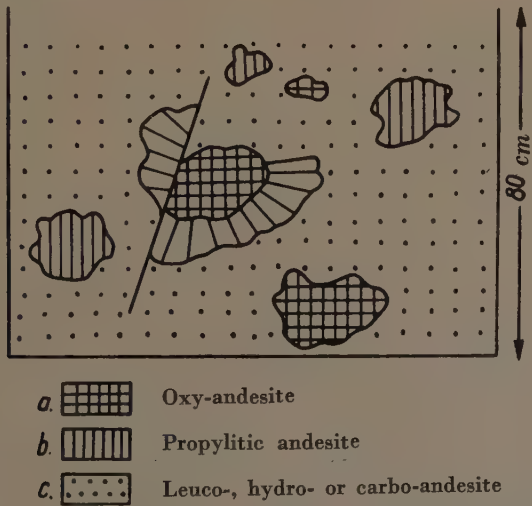
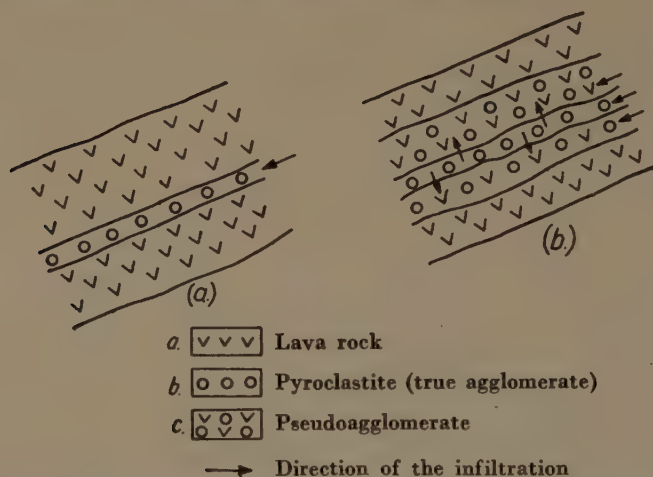


Fig. 11. Relation between propylite and oxy-andesite in pseudoagglomerates

This tectonical pseudoagglomerate is clearly distinguishable also from *pyroclastic agglomerates* with a lava-matrix. Such lava-matrix agglomerates or agglomeratic lavas [52] can be characterized, according to G. PANTÓ, as follows : 1. The agglomerate blocks and grains falling into the lava have a fluidal arrangement. 2. Agglomerate in some places is resorbed by the lava, and therefore shows concavities on the border line. 3. The blocks and grains of the agglomerate are weathered and form hollows in the harder lava cement. (On the contrary, in tectonical pseudoagglomerate, the greater, fresh, agglomerate-like parts are protruding from the soft, cement-like part.)

In a further stage of alteration, the apparent grain size may decrease to the degree of a *pseudotuff*. In accordance with G. PANTÓ, we are inclined to consider certain so-called ignimbrites, often described in many countries, as such pseudotuffs too :

According to the above-exposed concept, at least 5 kinds of pseudoagglomerates exist, namely structural lava breccia, flow lava breccia, pyroclastic agglomerate with a lava-matrix, pyroclastitoid deposits of lava- and other rock fragments, and the above-described metavolcanitic pseudoagglomerate. In our nomenclature, only the metavolcanitic pseudoagglomerates are called pseudoagglomerates, in the strict sense of the word.



12. Fig. Transformation of a pyroclastite horizon between two lava-banks (a) into pseudoagglomerate (b)

As structural movements are generally produced mostly along rock borders even originally showing great differences in rock solidity, the formation of pseudoagglomerates often takes place along the original pyroclastic tuff-agglomerate horizons intercalated among the broad benches of lava rocks. In this way, true agglomerate and pseudoagglomerate are often connected in space, whereby the recognition of agglomerate formation becomes difficult (Fig. 12). During the development of the volcanic subsidence structure, to be treated in Chapter VI, water-bearing pyroclastite horizons can be transformed into planes of structural movements and the development of pseudoagglomerate along these planes are considerably facilitated.

The identification of pseudoagglomerate even permits the determination of the main directions of postvolcanic structure, particularly the analysis of subsidence structure (see Chapter VI).

Some till now hardly understandable "irregular intrusions and blocks of effusive rocks in volcanic agglomerates and tuffs" represent evidently unal-

Table I

## Hypovolcanites

Magma  ↓	S u b v o l c a n i c					V o l c a n i c	
	crystallization	in clayey-sandy rock		in rocks with organic substances or in carbonate rocks		on moist rock	in water
		at high	low	at high	low		
		t e m p e r a t u r e					
Basaltic	Basic rocks with ore-peridotite	Chloro-dolerite	Carbo-dolerite	?	Analcite-basalt	Spilite ophiolite	
Andesitic	Effusive rocks with zoisitc-biotitic marginal facies	Hypovolcanitic propylite	Carbo andesite	Sulfo- and hydro-andesite			
Dacitic			Carbo-dacite	Sulfodacite hydrodacite			
Rhyolitic			?	?	(Perlite-pitchstone-pumice?)	Perlite pitches-pumice	





tered remainder of effusive rocks otherwise dominantly altered into pseudo-agglomerates or pseudotuffs. (Illustration e. g. in [64] and [65]).

12. The formation of hydrovolcanites accompanies the release of a considerable amount of *silicon*. Up to the present, opal, chalcedony, jasper, as well as quartzitized metavolcanites and hypovolcanites, and even some quartz dikes for the most part were considered as deriving from ascendant endogenous silicic solutions. As the overwhelming majority of these rocks are observable along meta- and hydrovolcanitic structural zones or dikes, it is obvious that they were for the most part formed exogenously, near the surface in connection with the formation of meta- and hydrovolcanites.

Thus the silicon released from feldspar-rocks by the formation of hydrovolcanites containing montmorillonite, illite and especially kaolinite is re-deposited in the *silicified rocks* and *veins of jasper, chalcedony* and *quartzite*. Hence the areal connection of deposits of ceramic minerals with silicified rocks and silica mineral veins, e. g. in the Mátra and Tokaj-Mountains.

13. In connection with hypovolcanitic phenomena of transvaporization, as well as with metavolcanitic metamorphism taking place along structural zones and dikes, heavy metal ions can also be dissolved from the country rocks of the environment. Such dissolved metallic elements of near-surface origin contribute to the formation of ore deposits too, as well as ascendant heavy-metal ions, bound incongruently in silicate magma and mobilized by their activation. In the case of precious metals, the near-surface exsolution process is considerably facilitated by oxidation (cf. the formation of a cementation zone). Trace-element concentration of some metals, e. g. that of gold, is higher in sedimentary rocks containing organic substances than in average igneous rocks. Therefore, a relatively large amount of precious metals can be dissolved from near-surface country rocks wherefrom they migrate, laterally or descending in the hypovolcanites and metavolcanites. Finally, they may precipitate around the crystal germs of ore minerals present in the ore veins. Therefore, some "*magmatic*" ore veins are not considered, at least partly, as monogenous formations of pure magmatic origin but as *polygenous ore deposits*, containing endogenous and exogenous ore substances. This conception is supported by our geoenergetical investigations too [39].

The above-described process may be efficient, especially in case of the so-called "young" or propylitic gold-silver formations.

The system of hypovolcanites and metavolcanites so far recognized, is shown in Table I, its position as function of water and silicium content, in Fig. 13.

## V. The origin of magmatic provinces

In the cases examined in the foregoing chapters the overwhelming majority of the water content of igneous rocks was proved as exogenous.

In turn it was impossible to detect in the same rocks any considerable quantity of internal magmatic water content.

Tests (e. g. by GORANSON [40]) on the water content of magma, do not give also the actual quantity of water present in the magma. They determine only the maximum of the possible hydration of the magma under different conditions.

JAGGAR [41] in one of his excellent papers on Hawaiian volcanism recently pointed out that the water present in lava does not represent any original plutonic product, but it is produced by the oxidation of hydrogen present in magma near to the surface.

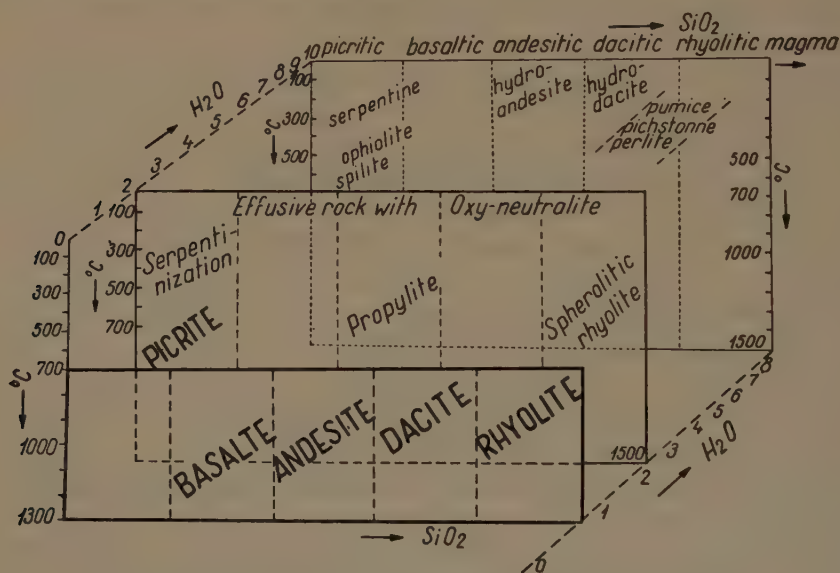


Fig. 13. The system of calc-alkaline, hypo- and metavolcanites

It is unlikely, even geoeenergetically, that low-potential hydrogen forming weak bonds, might surpass silicium and other high-potential ions in taking in considerable amounts of oxygen anions. OH-bonds and water can be principally produced, if the oxygen content of the magma increases chiefly near the surface, mostly by exogenous contaminations.

G. PANTÓ pointed out that, in the case of the Parícutín Volcano (Mexico) one had to take into consideration such an enormous amount of escaped water (44 000 000 t volatiles to 970 000 000 t lava) which could not be derived in a „juvenile” way from endogenous source [25].

Based on all these investigations, it seems probable that the majority of so-called “magmatic” water is of exogenous origin. This conception is also supported by geological considerations pointed out in the “Ver-

schluckungstheorie" of STAUB and in the concept of F. HORUSITZKY on the origin of so-called "internal water"[50].

Accordingly, we must return to a certain degree, to the assumption of "water-free" magma of BRUN, which was given up when the presence of water in the lava was proved. By the derivation of the water content of the lava from the transvaporization and from exogenous oxidation of hydrogen, a new light is thrown on the question and some passages of BRUN's argumentation become valid anew.

We briefly mention here also that in our opinion a partly exogenous derivation of the majority of other important volatiles of the magma — particularly that of carbon dioxide and sulphur compounds — is assumable too. In this respect we quote some references e. g. GERMANOV [42], besides the above-described features of carbovolcanites and metavolcanites.

In the present highly differentiated state of the earth's crust, it is quite unlikely that any considerable amount of volatiles might normally ascend from the depth in the (sub)volcanic belt of the orogenic regions. According to the conception elsewhere exposed [38], young magmas can hardly be derived from the residue of the primordial magmatic matter of the earth's crust, consequently young magmas are not of juvenile, but for the most part of anatectic origin. Accordingly, the majority of their volatile content is not of endogenous but of exogenous origin.

Thus, the development and the differentiation of the magma is considerably affected by the volatiles and other substances of exogenous origin. The silicic acid and alkalis in the course of transvaporization entering from the country rock into the magma, play a decisive part in the formation of the typical "pacific" andesite-rhyolite magmatic provinces of the folded zones, as well as in that of the biotite dioritic trondjemitic rock-series described by GOLDSCHMIDT as the differentiation series in moist environments. In this process, the role of real rock assimilation is less important than that of transvaporization.

Similarly in the development of alkali provinces, advanced by the assimilation of limestone, carbon dioxide transvaporization takes place first, and then leads to a real assimilation.

As for the formation of alkaline magmas by transvaporization, from subalkaline magmas we may quote the above-mentioned examples of spilitization, as well as that of the analcite-syenites, teschenites, alkali pegmatites, lugarites intercalated in diabase and peridotite sills, further the keratophyres of the Lahn district.

The potash trachyte of Telkibánya [55] may perhaps also be derived from a subalkaline rhyolitic magma, by particular exogenous transvaporization.

Thus the development and chemical composition of the magma is not predestined in the depth, but is considerably affected by the last environ-

ment in the stage of crystallization. The magma receives many characteristic components from its environment. This new conception points out that in the course of crystallization the magma not only gives off some substances to the country rocks but chiefly resorbes important components from the environment.

## VI. Tectonical investigation and structure of volcanic mountains

Physical changes taking place in volcanic rocks after the intrusion of magma, in consequence of cooling and on the effect of necessary tectonical processes are even more general, than the above-mentioned exogenous chemical changes of the same rocks.

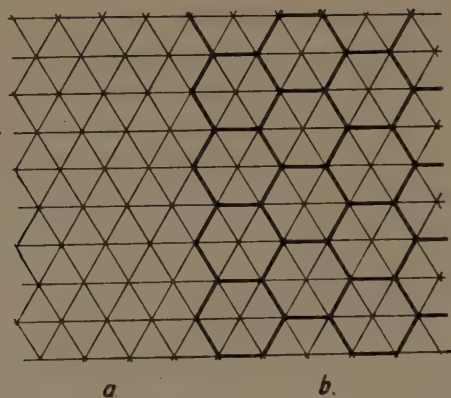


Fig. 14. Formation of a hexagonal columnar joint system by interruption of the three-direction fissuring

A) In connection with the cooling of magma (lava) a system of very fine contraction fissures is formed which, for the most part, is only subsequently activated into well-observable joints, on the effect of surface oxidation and hydration (weathering).

1. The extensive flows of basic, thin-liquid lavas, tend to contract in the principal direction of its extension, i. e. mainly horizontally, in consequence of bilateral cooling, acting on it from below and from above. Thus, a *vertical columnar joint* system with chiefly three-direction fissuring is formed. The formation of this system requires a minimum energy consumption, if it is developed by regular interruptions as shown in Fig. 14. In this way  $\frac{1}{3}$  as many fissures are produced as if the same fissures were continuous and, on the other hand, instead of  $60^\circ$ -edge-angle trigonal columns with six-pointed joint stars, there is produced a system of  $120^\circ$ -edge-angle hexagonal columns with only three-pointed joint-stars. In accordance with earlier suppositions,



cooling "centres" are really formed in plains normal to the columns, however, they are — at least partly — not the causes, but the consequences of columnar jointing.

Sometimes, a columnar jointing is observable in volcanic chimneys too. This can partly be parallel to the direction of the chimney, according to the observations of GY. VARJU and A. VIDACS. This can be the consequence of an intensive en-masse contraction of the chimney magma. The chimney is affected by the pressure of ascending magma in the active volcanic state, whereas, at cooling, not only this pressure ceases but a decrease in volume of the magma takes place too.

KLÜPFEL [15], on the other hand, has generally observed columnar joints normal to the surface (Fig. 15) thus he represented a system of horizontal columns in vertical chimneys (Fig. 16). This is presumably formed by a less intense contraction due to the cooling of the chimney-magma.

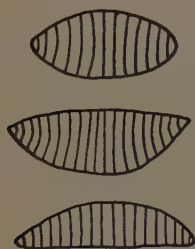


Fig. 15 Columnar joint of intrusive pillow-lava bodies, according to KLÜPFEL



Fig. 16. Columnar joint of intrusive basalt sill, according to KLÜPFEL

The columnar jointing of the chimneys and lava flows is not exclusively connected to basic lava. It can also appear in acid rocks becoming upon the effect of exogenous volatiles less viscous. (Plate II shows columnar-joint perlite of Pálháza. I thank Prof. L. TOKODY for this photograph.)

2. Viscous neutral magmas forming more isometrical masses than basalt-lavas are unidirectionally cooling. In the course of cooling, the marginal, cooler lamellae — parallel to the surface — segregate from the internal hotter parts. *Banked joints* of thicker andesitic lava flows, and on the upper margin of laccoliths are formed in this way. As unidirectional cooling is dominant on the margins of basic lava flows too, a margin of banked jointing may be produced in the latter, around the main columnar zone.

3. If the banked joint system is accompanied by a structural tensile stress, two systems of joints are formed, resulting in a *horizontal or oblique columnar jointing*. (E. g. andesite of Kopaszhegy near Tállya, Hungary.)

4. If the banked joint of cooling of the neutral lava is accompanied by the formation of two further systems of lithoclasts circa normally to each other, produced in consequence of structural compression, the directions of

lithoclasts, roughly normal to each other, result in a *cubic jointing*. The corners of the intersections of these three lithoclasts are less stable than the edges of intersection of only two lithoclasts. By the loosening of these corners, *spherical*



Plate II. Columnar joint of perlite

*jointing* is gradually developed, in consequence of hydration and variation in oxidation-reduction potentials, starting from the lithoclasts. This was described previously in coal [43], but is also valid for effusive rocks. In many cases, such volcanites of spherical joint were interpreted and mapped as pyroclastic agglomerates. The increased chemical effect accompanying spherical jointing often results in the formation of pseudoagglomerate as described on p. 220, see also fig. 17. The assumption of multiple eruption cycles e. g. in the Tokaj—Eperjes Mts. [45, 46, 47] is for the most part due to the fact that such pseudoagglomerates have been interpreted as horizons of true pyroclastites.

5. According to GY. VARJU, a system of *vertical fissures*, parallel to the direction of flow, can be formed in rhyolitic rocks, in accordance with the flow structures of viscous lava. It is likely that the partial evaporation of the moisture content on the surface contributes to the formation of such joint too. Vertical joints parallel to the direction of flow may also be developed in andesite, according to the observation of L. PESTY (e. g. Mount Sárhegy, near Gyöngyös).

B) On the basis of genetical interpretation of the lithoclasses of igneous rocks, we have elaborated a *method permitting to replace dip measures in volcanic rocks*. As already mentioned, the banked jointing formed by cooling is originally parallel to the surface, i. e. it is roughly as "horizontal" as the strata of sedimentary rocks. (According to the maximum  $33^\circ$  slope of volcanic

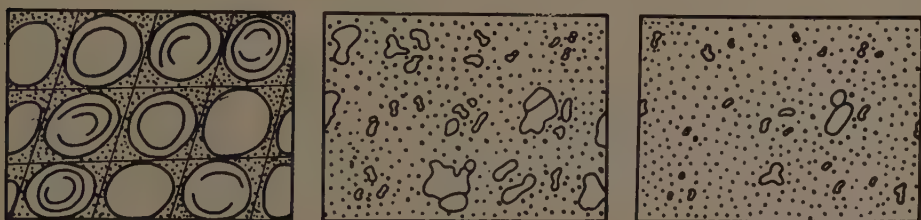


Fig. 17. Phases of the formation of pseudoagglomerate

cones, their dip remains, for the most part, below this value.) After the development of the tectonical structures of the territory, the slope of banked joints in lava rocks are determined by two components: the direction parallel to the original surface and the "structural" direction produced by subsequent dislocation. In the same way, as structure may be determined on the basis of the dips of sedimentary strata, the structure of volcanic mountains and the mutual relation of its lava formations may be traced to the slope directions of lava-rocks showing banked joints.

For a systematic application of this method, it was necessary to elucidate the genesis of different volcanic lithoclasses, to distinguish banked joints from other kinds of lithoclasses, to examine the oscillation of the slope directions of banked joints, as determined by the original surface, and to compare these directions with the adjacent true dips, measured on sedimentary strata. On an average, we have found a maximum  $\pm 45^\circ$  variation in the joint direction of lava banks, whereas the agreement of their averages with the true dips of sedimentary strata was measured within  $\pm 15^\circ$ . On the basis of all these, the measure of banked jointing is applicable with sufficient accuracy for the evaluation of structural relations.

The measurement of slope directions of banked jointing of lava rocks give dynamic data, permitting a rapid and reasonable geological mapping of

volcanic mountains, and the determination of their structure. This method giving good results was repeatedly employed by us and our collaborators.

C) By this new method we have succeeded in determining the outlines of the structural relations of three volcanic mountains in Hungary. In all three cases we found negative structures, contrary to the structure of active volcanoes.

Such structures may be interpreted as *subsidence structures*. The negative pressure resulting from the exhaustion of magma in the chamber, produces a major depression structure. The volcanic subsidence is sometimes observable on the surface, as caldera. Mostly a single, abrupt, high-matter-supply eruption, with abundant gas content and not too deep magma chamber is required for the formation of calderas. The classification of such volcanic basins was given by R. A. DALY [11]. However, the collapse of a deep chamber appears for the most part later on the surface, its effect being upwards gradually decreasing. Because of the synchronous volcanic refilling of the surface, the subsidence character of such a structure is observable only after some denudation. Similarly, slow caldera formation according to repeated or almost continuous eruptions does not strikingly appear on the surface (Hawaii, Vesuvius) [49]. Deep, short-living volcanic activity from deep magma chambers can also produce subsequent depressions without any caldera formation.

Consequently, the volcanic-subsidence structure seems to be a quite general phenomenon — much more general than the caldera-structure — and results in an intensive metavolcanitic alteration of the volcanic rocks. "Magmatic" mineralization i.e. the formation of subvolcanic ore deposits may obviously be related to the formation of such structures.

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## ÜBER DIE PETROLOGIE DER VULKANITE UND DIE WECHSELWIRKUNG VON MAGMA UND WASSER

E. SZÁDECZKY-KARDOSS

### Zusammenfassung

Neue Untersuchungen in der tertiären Vulkanzone der Karpaten führten zur Erkenntnis einer sehr verbreiteten Rückwirkung der sandig-tonigen, mergeligen und pyroklastischen Nebengesteine sowie Kohlen auf das Magma. Diese Rückwirkung, die als *Transvaporisation* bezeichnet wird, vermag die chemische Zusammensetzung und Differentiationsrichtung sogar von mächtigen Magmakörpern grundsätzlich ändern. Gesteine, wie gewisse Propylite, Analzimbassalte, Analzimbassalte, Crinanite, Teschenite, Weiburgite, Lahn-Keratophyre, Alkalipegmatite, Lugarite, Analzimsyenite, sowie Perlite, Pechsteine, Bimssteine u. a. m. entstehen teils oder gänzlich unter Mitwirkung dieses Prozesses. Sie stellen keine gewöhnliche Orthomagmatite, sondern Gesteine dar, die durch eine starke Ausbreitung der Kristallisationstemperatur bis ins hydrothermale Bereich entstanden sind. Sie werden als *Hypomagmatite* bezeichnet.

Andererseits werden systematische nachträgliche Umwandlungen der Vulkanite besprochen und dabei neue Gesteinstypen, wie Oxymetavulkanite, Leukovulkanite, Chloro- und Hydrovulkanite, sowie Pseudoagglomerate usw. — insgesamt *Metamagmatite* — beschrieben.

Die Bedeutung dieser neuen Begriffe bezüglich der Systematik der Magmatiten wird kurz ebenfalls erörtert.

Die Entstehung dieser Gesteine steht in enger Beziehung zur Entwicklung verschiedener Kluftsysteme der Vulkanite, deren systematisch-genetische Beschreibung ebenfalls versucht wird.

Da diese Arbeit als Einleitung zur neuartigen Untersuchung der (sub)vulkanischen Gebirge bestimmt ist, wird schließlich der Einsenkungsbau der Vulkangebirge besprochen und eine neue Methode zur tektonischen Untersuchung solcher Gebirge vorgeschlagen.

## О ПЕТРОЛОГИИ ВУЛКАНИЧЕСКИХ ПОРОД И О ВЗАИМОДЕЙСТВИИ МАГМЫ И ВОДЫ

Э. САДЕЦКИ-КАРДОШ

*Резюме*

Исследования, проведенные в последнее время в третичной вулканической зоне Карпат, привели к познанию широкораспространенного противодействия песчано-глинистых, мергелистых и пирокластических боковых пород и угля на магму. Это противодействие, названное автором «грансвапоризацией», может принципиально изменять химический состав и направление дифференциации даже громадных магматических тел. Некоторые горные породы, как напр. отдельные пропилиты, анальцимовые базальты, анальцимовые диабазы, кринаниты, тешениты, вейльбургиты, лан-кератофиры, щелочные пегматиты, лугариты, анальцимовые сиениты, а также перлиты, смолистые камни, пемзы и др. частью или полностью образовались при содействии указанного процесса. Они не представляют собой обычные ортомагматиты, а горные породы, возникшие вследствие значительного распространения кристаллизационной температуры до гидротермальной области. Они называются гипомагматитами.

В дальнейшем обсуждаются систематические последовательные превращения вулканитов, причем описываются новые типы горных пород, как напр. оксиметавулканиты, лейковулканиты, хлоро- и гидровулканиты, а также псевдоаггломераты и пр. — в общем метаматиты.

Вкратце также излагается значение этих новых понятий в отношении систематики магматитов.

Возникновение указанных горных пород находится в тесной связи с развитием различных трещинных систем вулканитов, систематическое генетическое описание которых также попытается.

Так как настоящая статья представляет собой ввод к новым исследованиям (суб-)вулканических гор, в заключении обсуждается прогибное строение вулканических гор и описывается новый метод тектонического изучения таких гор.





# MICROSEISMICAL EVALUATION OF THE EARTHQUAKE OF JANUARY 12, 1956, AND THE CRUSTAL STRUCTURE OF THE HUNGARIAN BASIN

By

E. BISZTRICSÁNY and D. CSOMOR

EÖTVÖS UNIVERSITY, BUDAPEST

The shock originated at Dunaharaszti on the 12th of January, 1956, permitted the determination of the crustal structure below the Hungarian Basin. According to results, the "granitic" layer lying below the sedimentary strata extends to a depth of 20,2 km, whereas the bottom of the "gabbroic" layer lies at a depth of 33 km. The velocities computed for the waves of the shock are in good agreement with the internationally used values determined elsewhere. The agreement is especially good for the  $P_n$  wave. The focus depth of 3,31 km indicates that the shock was not generated in the crust itself but rather in the sedimentary basement of the basin consisting of massive limestones; most probably as a consequence of the rejuvenation of a fault line. This process is generally characteristic of the Hungarian basin.

The earthquake originated at 0,6<sup>h</sup> 46<sup>m</sup> 09,3<sup>s</sup> (C. E. M. T.) in the morning of the 12th of January, 1956 at Dunaharaszti, S of Budapest, was registered by seismic stations at distances as great as 2000 km. The European stations gave good registrations. A magnitude of 5,6 was computed from the seismogram of the Prague Anderson—Wood instrument. The preliminary macroseismical evaluation gave for the epicenter a strength of 7,5 according to the Mercalli—Sieberg scale.

In the following an attempt is made to determine the structure and dimensions of the crust below the Hungarian Basin with the aid of this shock.

As the most intense effect was restricted to a very small area, the macroseismically determined epicenter is regarded as the true one. The center of the most severely shocked area is characterized by the geographical coordinates 47°21' N, 19°04' E. This is the very epicenter. The distance of the stations evaluated was computed by the formula

$$\cos \Delta_n^\circ = X_0 X_n + Y_0 Y_n + Z_0 Z_n,$$

$\Delta_n^\circ$  signifying the epicentral distance, and the further symbols being given by

$$X_n = \cos \varphi_n \cos \lambda_n$$

$$Y_n = \cos \varphi_n \sin \lambda_n$$

$$Z_n = \sin \varphi_n$$

$\varphi_n$  is herein the geographical latitude,  $\lambda_n$  the longitude of the station. The zero index refers to the epicenter (Fig. 1).

The equation

$$\sqrt{\Delta_n^2 + h^2} = V_{\bar{P}} (t_n - t_0) \quad (1)$$

was applied to determine the relation of the speed of propagation of the direct wave, ( $V_{\bar{P}}$ ), to origin time, ( $t_0$ ), focus depth ( $h$ ) and arrival time ( $t_n$ ).

The data of seven of the available seismograms were utilized. Thus seven equations were obtained for three unknowns. Because of this, the determination



Fig. 1. Distribution of the stations whose data were utilized in evaluating the shock of January 12, 1956. The cross indicates the epicenter

of the unknowns was not unequivocal and the correct values had to be determined by compensation computation. Equation (1) can be written into the form

$$F_n = \frac{1}{V_{\bar{P}}} \sqrt{\Delta_n^2 + h^2} + t_0 - t_n = 0, \quad (2)$$

$F_n$  being a quadratic function of three variables that can be linearized by evolution into a series, in order to permit the application of the method of least squares. Let us note the approximate values of velocity, depth and time with  $V'_{\bar{P}}$ ,  $h'$  and  $t'_0$ , and the corrections with

$$\zeta = h - h'$$

$$\tau = t_0 - t'_0$$

$$\nu = v_{\bar{P}} - v'_{\bar{P}}$$

then

$$F_n = F_{n_0} + \frac{\partial F_{n_0}}{\partial v_{\bar{p}}} \nu + \frac{\partial F_{n_0}}{\partial h} \zeta + \frac{\partial F_{n_0}}{\partial t_0} \tau = 0, \quad (3)$$

the zero index indicating the value of the function at the approximated point. Introducing the abbreviations

$$\begin{aligned} \frac{\partial F_{n_0}}{\partial v_{\bar{p}}} &= c_n, \quad \frac{\partial F_{n_0}}{\partial h} = b_n, \quad \frac{\partial F_{n_0}}{\partial t_0} = a_n \\ F_{n_0} &= l_n \end{aligned} \quad n = 1 \dots 7$$

(3) obtains the form

$$F_n = a_n \tau + b_n \zeta + c_n \nu + l_n \quad (4)$$

The partial derivatives of (2) are

$$\begin{aligned} a_n &= \frac{\partial F_{n_0}}{\partial t_0} = 1 & b_n &= \frac{\partial F_{n_0}}{\partial h} = \frac{1}{v_{\bar{p}}'} \frac{h'}{\sqrt{\Delta_n^2 + h'^2}} \\ c_n &= \frac{\partial F_{n_0}}{\partial v_{\bar{p}}} = -\frac{1}{v_{\bar{p}}'^2} \sqrt{\Delta_n^2 + h'^2} & \text{and} \\ l_n &= \frac{1}{v_{\bar{p}}'} \sqrt{\Delta_n^2 + h'^2} + t_0' - t_n & n = 1 \dots 7 \end{aligned}$$

The error equation system can be derived out of (4):

$$v_n = a_n \tau + b_n \zeta + c_n \nu + l_n \quad n = 1 \dots 7$$

Applying the method of least squares, the normal equation system is obtained. With the notations of Gauss,

$$\begin{aligned} [a a] \tau + [a b] \zeta + [a c] \nu + [a l] &= 0 \\ [a b] \tau + [b b] \zeta + [b c] \nu + [b l] &= 0 \\ [a c] \tau + [b c] \zeta + [c c] \nu + [c l] &= 0 \end{aligned}$$

The solution of the equation system yields the corrections to be applied to the approximated values. The middle errors of the individual corrections and consequently the errors of the shock parameters are then

$$m_\tau = \sqrt{\frac{[v v]}{(n-m)}} Q_{11}; \quad m_\zeta = \sqrt{\frac{[v v]}{(n-m)}} Q_{22}; \quad m_\nu = \sqrt{\frac{[v v]}{(n-m)}} Q_{33}$$

$n$  denoting the number of stations,  $m$  that of unknowns.  $Q_{11}$ ,  $Q_{22}$  and  $Q_{33}$  are the solutions of the weighting equations.

For the first compensation of the direct wave the authors used the  $V_{\bar{p}}$  velocity value 5,5 km/sec on the basis of literature data, the  $h$  value 10 km by preliminary macroseismic evaluation, and the value 9,3 sec as an approximation of origin time, as obtained by compensating the equation

$$S_n - P_n = (K - 1) (P_n - t'_0)$$

on the basis of the data of the stations listed below.

Station	$P_n$	$S_n$	$S_n - P_n$
Jena	06 47 40,1	06 48 53,7	73,6
Zagreb	46 53,3	47 26,9	33,6
Beograd	46 53,0	47 30,4	37,4
Câmpulung	47 23,8	48 17,1	53,3
Bacău	47 32,5	48 31,3	58,8

The coefficients of the normal equation thus become

$$[a a] = 5 \quad [a b] = 256,7 \quad [a l] = 382,7 \quad [b b] = 14243,0; \quad [b l] = 21046,0.$$

The value  $t'_0 = 9,3$  sec was obtained for the solution of normal equations.

The compensation of  $h$ ,  $V_{\bar{p}}$  and  $t_0$  values was performed by utilizing the data of the stations listed in the following table.

Station	$A_n(\text{km})$	$t_n$
Budapest (W) .....	16,3	06 46 12,3
„ (Kr) .....	20,0	13,0
Kecskemét .....	69,1	21,3
Hurbanovo .....	86,7	25,4
Kalocsa .....	89,2	25,6
Wien .....	240,8	52,5
Câmpulung .....	495,3	47 39,9

The arrival times of the stations within the Carpathian Basin were corrected with 0,6 sec because of the loose sediments of 1,3 km average thickness and 2,2 km/sec seismic velocity determined by practical seismic investigations. The Câmpulung data were, however, left uncorrected, as this station is built on the basement of the Carpathians.

The first compensation yielded too great a correction for focus depth ( $\zeta = -7,6$  km). Therefore the compensation was performed again with the



approximate values  $h' = 3$  km,  $t'_0 = 9,3$  sec and  $V_P^- = 5,5$  km/sec. The coefficients thereby obtained are seen below.

Station	$a_n$	$b_n$	$c_n$	$l_n$
Budapest (W) .....	1	0,0319540	— 0,56430	0,1038
„ (Kr) .....	1	0,0263250	— 0,68497	0,0673
Kecskemét .....	1	0,0078870	— 2,28630	0,5750
Hurbanovo .....	1	0,0062877	— 2,86780	— 0,3270
Kalocsa .....	1	0,0061116	— 2,95050	— 0,0010
Wien : .....	1	0,0022650	— 7,96100	0,5870
Câmpulung .....	1	0,0010936	— 16,37300	— 0,5420

The normal equation system thus becomes

$$\begin{aligned}
 7\tau + 0,81924 \zeta - 33,688 \nu + 0,4631 &= 0 \\
 + 0,0018688 \zeta - 0,12622 \nu + 0,0082974 &= 0 \\
 + 354,4 \nu + 3,7231 &= 0
 \end{aligned}$$

Its solution will be

$$\begin{aligned}
 \zeta &= (-0,99 \pm 1,10) \text{ km} \\
 \nu &= (-0,012 \pm 0,024) \text{ km/sec} \\
 \tau &= (-0,01 \pm 0,03) \text{ sec}
 \end{aligned}$$

Consequently, focus depth is  $h = (3,31 \pm 1,10) \text{ km}$

origin time  $t_0 = (9,29 \pm 0,03) \text{ sec}$

propagation velocity of the direct wave  $V_P^- = (5,49 \pm 0,024) \text{ km/sec}$ .

To be able to compute the depth of discontinuity surfaces it is further necessary to know the speed of propagation of the  $P^*$  and  $P_n$  waves in the corresponding layers, as determined from the travel-time curve.  $P_n$  is the wave refracted at the Mohorovičić discontinuity,  $P^*$  that refracted at the Conrad surface.

The data utilized to compensate the wave are as follows :

Station	$\Delta_n$	$t_{p^*}$
Wien .....	240,8	06 46 48,6
Bacău .....	607,7	47 40,5
Jași .....	646,6	47,4

The normal equations become

$$\begin{aligned} 3b + 1495,1 \text{ m} + 256,5 &= 0 \\ + 845375,5 \text{ m} + 142221,6 &= 0 \end{aligned}$$

The solutions are

$$V_{P^*} = -\frac{1}{m} = (6,975 \pm 0,003) \text{ km/sec},$$

$$b = (-13,99 \pm 1,07) \text{ sec.}$$

The compensation data for the  $P_n$  wave were :

Station	$\Delta_n$	$t_{P_n}$
Szeged .....	156,6	06 46 34,8
Wien .....	240,8	45,6
Zagreb.....	287,7	53,3
Beograd .....	300,0	53,0
Câmpulung .....	495,3	47 23,8
Bacău .....	607,7	32,5
Jasi .....	646,6	35,7
Jena.....	674,4	40,1

The system of normal equations was

$$\begin{aligned} 8b + 3409,1 \text{ m} + 558,8 &= 0 \\ + 1745807,8 \text{ m} + 274757,9 &= 0 \end{aligned}$$

The solutions were

$$V_{P_n} = -\frac{1}{m} = (8,182 \pm 0,005) \text{ km/sec}$$

$$b = (-18,01 \pm 2,26) \text{ sec.}$$

The travel time of the wave refracted at the Conrad discontinuity from the focus to the station is given by

$$t_{P^*} - t_0 = \frac{2d_1 - (h - 1,3)}{V_{\bar{P}} \cos i} + \frac{\Delta_n - [2d_1 - (h - 1,3)] \operatorname{tg} i}{V_{P^*}}$$

The travel time of the wave refracted at the Mohorovičić discontinuity is

$$t_{P_n} - t_0 = \frac{2d_1 - (h - 2,6)}{V_P \cos i_1} + \frac{2d_2}{V_{P^*} \cos i_2} + \frac{\Delta_n - 2d_2 \operatorname{tg} i_2 - [2d_1 - (h - 2,6)] \operatorname{tg} i_1}{V_{P_n}}$$

On substituting the computed values one obtains

$$d_1 = (18,9 \pm 3,7) \text{ km}$$

$$d_2 = (12,8 \pm 1,2) \text{ km.}$$

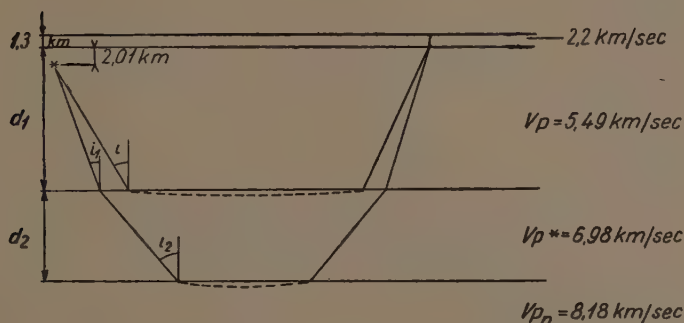


Fig. 2. The path of the refracted waves

The compensation of the transversal  $\bar{S}$  wave was based upon following data :

Station	$\Delta_n$	$t_{\bar{S}}$
Beograd .....	300,0	06 47 47,0
Câmpulung .....	495,3	48 42,7
Jași .....	674,4	49 32,3

The normal equations are

$$3b + 1469,7 m + 481,0 = 0$$

$$+ 790137 m + 255186 = 0$$

Hence

$$V_{\bar{S}} = -\frac{1}{m} = (3,586 \pm 0,002) \text{ km/sec}$$

$$b = (-23,7 \pm 1,1) \text{ sec.}$$

No  $S^*$  wave was observed in the seismograms and consequently no wave velocity was computed.

The compensation of the  $S_n$  wave :

Station	$\Delta_n$	$t_{S_n}$
Zagreb.....	287,7	06 47 26,9
Beograd .....	300,0	30,4
Câmpulung .....	495,3	48 17,1
Bacău .....	607,7	31,3
Jena.....	674,4	53,7

Normal equations :

$$5b + 2365,1 m + 339,4 = 0$$

$$+ 1242207 m + 187211,8 = 0.$$

Hence

$$V_{S_n} = -\frac{1}{m} = (4,62 \pm 0,003) \text{ km/sec}$$

$$b = (-25,5 \pm 4,73) \text{ sec.}$$

The equations of the travel-time curves are

$$\bar{P} \text{ wave: } t_{\bar{P}} = \frac{\Delta}{5,49} \sqrt{\Delta^2 + 3,31^2} + 9,29$$

$$P^* \quad ,, \quad t_{P^*} = \frac{\Delta}{6,98} + 13,99$$

$$P_n \quad ,, \quad t_{P_n} = \frac{\Delta}{8,18} + 18,01$$

$$\bar{S} \quad ,, \quad t_{\bar{S}} = \frac{\Delta}{3,59} + 23,7$$

$$S_n \quad ,, \quad t_{S_n} = \frac{\Delta}{4,62} + 25,5$$



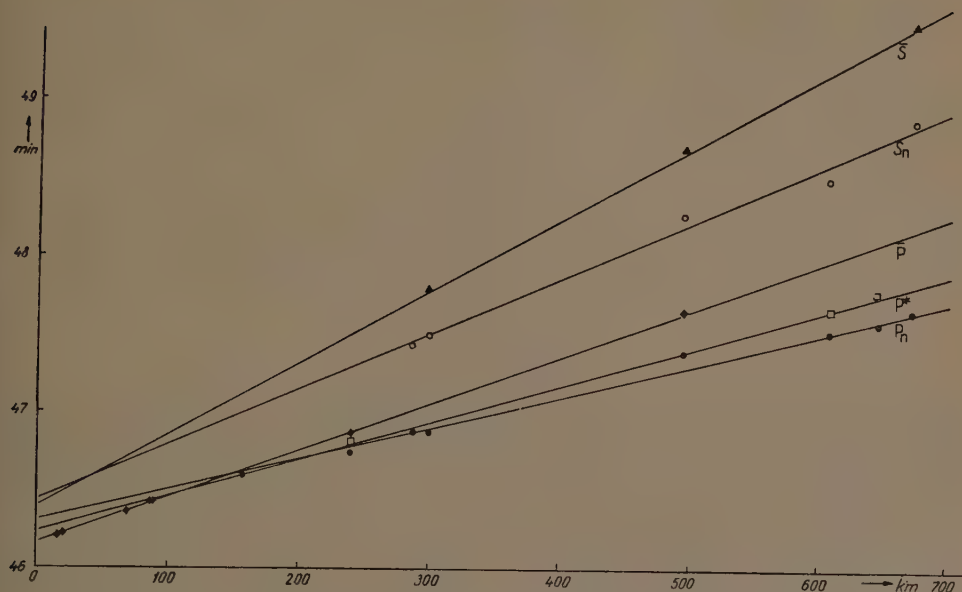


Fig. 3. Travel-time curves of the shock of January 12, 1956

The table below gives opportunity for comparing our results with those obtained at the Heligoland and Haslach blasts.

	Carpathian Basin	Heligoland	Haslach
$V_{\bar{P}}$ .....	5,49 km/sec	5,60 km/sec	5,9— 6,0 km/sec
$V_{P^*}$ .....	6,98 „	6,40 „	6,55 „
$V_{P_n}$ .....	8,18 „	8,20 „	8,20 „
$V_{\bar{S}}$ .....	3,59 „	2,94 „	
$V_{S_n}$ .....	4,62 „	4,40 „	
Conrad surface .....	20,20 km	10,70 km	20,00—22,00 km
Mohorovičić surface .....	33,00 „	27,40 „	29,00—33,00 „

A thickness increase from Heligoland towards Haslach was established on the basis of the Germany blasts. This thickening seems to continue towards the Carpathian Basin as well.

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# MIKROSEISMISCHE BEARBEITUNG DES ERDBEBENS VOM 12. JANUAR 1956 UND DIE STRUKTUR DER ERDKRUSTE IM GEBIETE DES UNGARISCHEN BECKENS

Von

E. BISZTRICSÁNY und D. CSOMOR

## Zusammenfassung

Das am 12. Januar 1956 in der Umgebung von Dunaharaszti stattgefundenere Erdbeben ermöglichte die Bestimmung der Struktur der Erdkruste im Gebiete des Ungarischen Beckens. Auf Grund der erzielten Ergebnisse reicht die unter der sedimentären Hülle gelagerte "Granitkruste" bis zu einer Tiefe von 20,2 km herab, während sich das Liegende der "Gabbrokruste" in einer Tiefe von 33 km befindet. Die aus dem Erdbeben für die seismischen Wellen berechneten Geschwindigkeitswerte stimmen mit den in anderen Gebieten gemessenen und international angewendeten Angaben gut überein. Besonders gut ist die Übereinstimmung im Falle der  $P_n$ -Welle. Die 3,31 km betragende Tiefe des Herdes weist darauf hin, dass das Erdbeben nicht der Erdkruste selbst, sondern den den Beckenboden bildenden massiven Kalksteinen entsprang, u. zw. aller Wahrscheinlichkeit nach als Folge der Erneuerung einer Störungslinie. Dieser Vorgang ist für das Ungarische Becken allgemein bezeichnend.

# МИКРОСЕЙСМИЧЕСКАЯ ОБРАБОТКА ЗЕМЛЕТРЯСЕНИЯ 12 ЯНВАРЯ 1956 г И СТРОЕНИЕ КОРЫ ВЕНГЕРСКОГО БАСЕЙНА

Э. БИСТРИЧАНЬ и Д. ЧОМОР

## Резюме

Землетрясение, имевшее место 12 января 1956 г. в окрестности с. Дунахарасти, допустило определение строения коры на территории Венгерского бассейна. По полученным данным «гранитовая» кора под осадочным слоем распространяется до глубины 20,2 км, в то время как подошва «габбровой» коры находится на глубине 33 км. Величины скоростей, рассчитанные из землетрясения, хорошо совпадают с международными данными, измеренными в других областях. Особенно хорошим является совпадение в скорости волны  $P_n$ . Глубина очага землетрясения, располагающегося на глубине 3,31 км, указывает на то, что землетрясение выскочило не из самой коры, а из подошвы бассейна, построенной карбонатными породами, по всей вероятности вследствие возобновления одной из сбросовых линий.

# GEOTHERMIC INVESTIGATIONS IN THE HUNGARIAN PLAIN

By

T. BOLDIZSÁR,

POLYTECHNICAL UNIVERSITY, SOPRON

The statistical interpretation of the outflow temperatures of 431 wells scattered on the Hungarian Plain and the correction of temperatures, made it possible to ascertain the average gradient of temperature of this territory. The average gradient was found to be  $4,76 \cdot 10^{-4}$  deg. C/cm. The temperature survey in ten wells reaching 2000 m in depth showed that this gradient seems to be rather the lower limit as the average gradient values were between 5 and  $7 \cdot 10^{-4}$  deg. C/cm. Assuming the average value of conductivity of the Tertiary strata building up this basin 0,004 cgs, the average terrestrial heat flow is at least  $1,9 \cdot 10^{-6}$  cal/cm<sup>2</sup>, sec and it is probable that the average value is higher and can be taken about  $2,4 \cdot 10^{-6}$  cal/cm<sup>2</sup>, sec.

As it is well known, the Hungarian Plain may be considered as a basin surrounded mainly by Mezozoic and Palaeozoic mountains. The bottom of the basin is formed by primary Mezozoic, but in some places Paleozoic rocks, gradually sunk to a depth of 3000 m, and in some places even deeper, was filled up by Tertiary sedimentary formations, mainly Miocene and Pliocene clays, marls, sand- and limestones, moreover there are, chiefly in its Northern part, Eocene and Oligocene strata (Fig. 5.) This basin has been well known since the second part of the last century for its small geothermic gradient.

But up to now there have been no measurements concerning the value of the terrestrial heat flow, i.e. the quantity of heat streaming from the interior of the earth to its surface. Though we are in possession of numerous data of temperature measurements, the thermal conductivity of the strata has not been measured up to now.

SÜMECHY in the 'twenties of this century measured on the Hungarian Plain (Fig. 1) the temperature of the water flowing out of 431 artesian wells and in 1929 published the data of measurement and their interpretation [1]. The same series of measurements were interpreted in 1953 by SCHEFFER and KÁNTÁS too [2]. The fundamental error of both interpretations is that in the calculation of the temperature gradient of the wells, bored to a depth of 20—460 m, the depth of the so-called neutral stratum (about 20 m under the surface) was deduced from the depth of the water supplying stratum, and therefore the values of the gradient of temperature, especially when calculated for wells of small depth, were too high and considerably differ from their true value.

Furthermore, the cooling down of the water flowing upward in the wells has not been taken into consideration and therefore smaller values were calculated for the gradient of temperature. In 1956 I investigated the temperature distribution of flowing wells, and the correction of temperature for virgin rock temperature [3] and applied the results to obtain the geothermic correction of one of the wells on the plateau of the Colorado [4]. With the aid of the result, the virgin rock temperatures can be calculated from the temperature

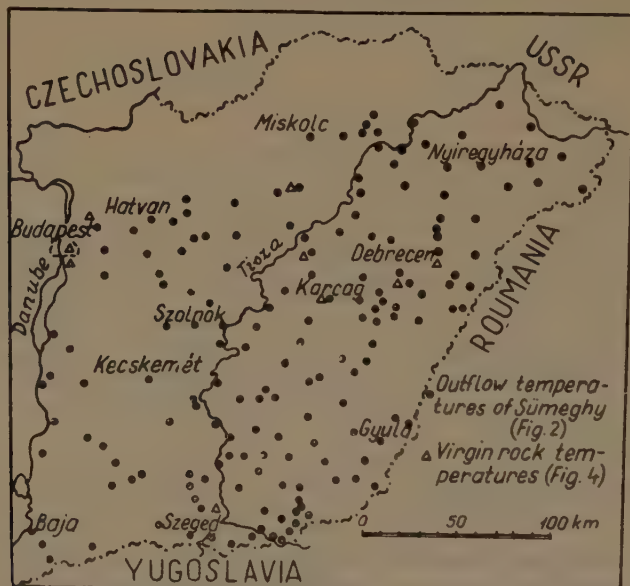


Fig. 1

of the outflowing liquid. According to it, the true temperature gradient from the differences in temperature ( $\tau$ ) between the liquid and the rock, measured on the surface, is

$$\sigma = \frac{\lambda \cdot F(\psi) \tau}{V \cdot c \left[ 1 - \exp \left( - \frac{\lambda F(\psi) H}{V \cdot c} \right) \right]} \quad (1)$$

where  $V$  is the quantity of liquid flowing in the well;  $c$  is the specific heat of the liquid;  $H$  the depth of the water-supplying stratum;  $\lambda$  is the equivalent thermal conductivity of the rocks.

$$F(\psi) = \frac{8}{\pi} \int_0^{\infty} \frac{e^{-\psi \beta^2}}{J_0^2(\beta) + Y_0^2(\beta)} \frac{d\beta}{\beta} \quad (2)$$



where  $\psi = \frac{at}{R^2}$ ;  $a$  is the thermal diffusivity;  $t$  is the time elapsed from the start of the liquid flow;  $R$  is the radius of the borehole;  $\beta$  is the variable of the integral,  $J_0$  and  $Y_0$  are Bessel-functions of the first and second kinds of zero order; the value for  $F(\psi)$  can be made up from the charts [5].

To compute the correction of the original measurements carried out by SÜMEGHY, some necessary data are lacking, as for instance: the thermal con-

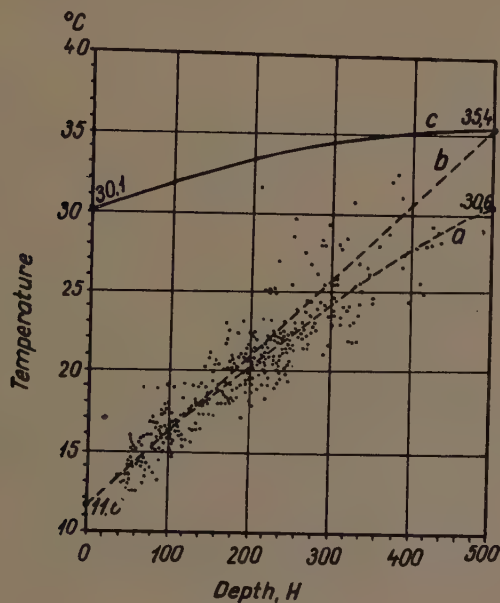


Fig. 2

ductivity of the strata, the quantity of water, the time elapsed from the start of the liquid flow and so on, therefore the geothermic correction for each individual well cannot be made.

The outflow temperature data given by SÜMEGHY have been recently statistically treated by STEGENA [6]. On the basis of the data of measurement the best fitting cubic parabola was calculated (Fig. 2“a”) further the gradient of temperature ( $\sigma$ ) as a function of depth. It was found that its value extrapolated to the surface is  $4,76 \cdot 10^{-4}$  °C/cm, while it decreasing in depth of 500 m to  $3,71 \cdot 10^{-4}$  °C/cm. The value of the so-called geothermical gradient (gg) is of 21,0 and 27,0 m/°C, respectively. The relation of the gradient to the depth is parabolical (Fig. 3). The values gained in this way are average values, and can be considered as average values for the whole of the Hungarian Plain.

The authors [1, 2, 6] we referred to, interpreted the change of gradient in such a way that it decreases with the depth, and they came to the conclusion

that there must be "geothermal zones" and "geothermal anomalies". There is no need for these assumptions.

Assuming that the decrease of the gradient appears as a consequence of the lack of correction it may be concluded that the calculations are not based on real, but on apparent gradients i. e. on the temperature of the water flowing out which may considerably differ from that of virgin rock. With the help of this assumption it is possible to make the correction. Quoted from my work

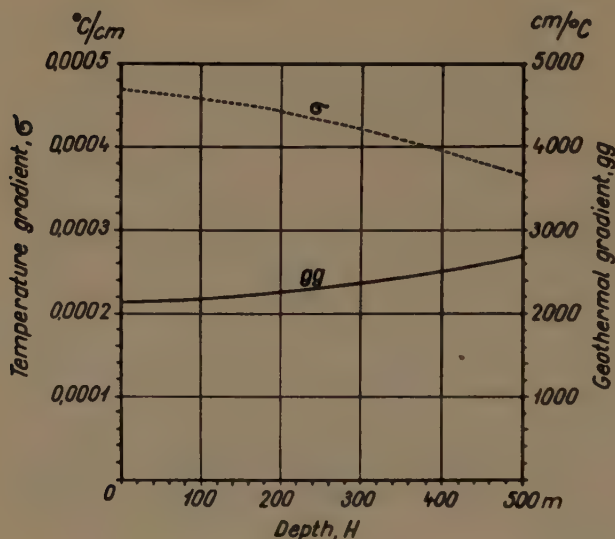


Fig. 3

[3] the value of the correction of the gradient of temperature can be calculated from the apparent gradient  $\sigma_{app}$ , relative to the depth of the inflow of water on the basis of the following relationship

$$\psi = \frac{\lambda \cdot F(\psi) \cdot H}{V \cdot c \left[ 1 - \exp \left( - \frac{\lambda \cdot F(\psi) H}{V \cdot c} \right) \right]} \quad (3)$$

where  $\psi = \frac{\sigma}{\sigma_{app}}$  and the true gradient is

$$\sigma = \psi \cdot \sigma_{app}. \quad (4)$$

It can be assumed from these results that theoretically the true gradient can be measured, where there is no correction caused by the cooling down

of the water, i. e. on the surface, and it is obvious that the true value of the gradient is the extrapolated value of the  $\sigma$ -curve on the surface. As the value of  $\sigma_{\text{app}}$  is known from Fig. 3, the value for  $\Psi$  in a depth of 500 m is :

$$\Psi = \frac{4,76 \cdot 10^{-4}}{3,71 \cdot 10^{-4}} = 1,283$$

On this basis from Eq. 3 the value of  $\varepsilon = \frac{\lambda \cdot F(\psi)}{V \cdot c}$  may be calculated :

$$\varepsilon H = \Psi [1 - \exp(-\varepsilon H)] \quad (5)$$

Eq. 5 cannot be solved with  $\varepsilon$ , but its value can be calculated by the way of approximation. Its value is :

$$\varepsilon = 0,00106.$$

From this value an average quantity of liquid can be calculated, if we possess some basis for the values of  $\lambda$  and  $t$ . It must be remembered that the average quantity of liquid — on the basis of STEGENA's calculations — is the quantity of liquid in an idealized well, bored through the thermal conducting stratum, typical of the average conditions for the Hungarian Plain. Accepting values for  $\lambda$  between 0,03 and 0,05 cgs, respectively, as upper and lower limiting values, furthermore, fixing the value for  $t$  with  $3,6 \cdot 10^7$  and  $3,6 \cdot 10^8$  sec as possible lower and upper limits, the value of the quantity of liquid in the ideal well can be computed with the following equation

$$V = \frac{\lambda \cdot F(\psi)}{\varepsilon \cdot c} \quad (6)$$

Table I gives the volume rate of water in  $\text{cm}^3/\text{sec}$ , taking finally into consideration the average radius of the casing equal to  $R = 10$  cm.

Table I

<div style="display: inline-block; transform: rotate(-45deg);"> <math>\lambda</math>  <math>t</math> </div>	0,003	0,005
	cal/cm · sec · °C	
	V cm <sup>3</sup> /sec	
sec		
$3,6 \cdot 10^7$	383	366
$3,6 \cdot 10^8$	381	288

According to Table I, the thermal conductivity is of little effect on the value of the quantity of water, while the presumed time (14 months, and 11,4 years, respectively) has a much greater effect on the results of the calculations. The probable quantity of water is about  $330 \text{ cm}^3/\text{sec}$ .

In Fig. 3 the exponential curve "c" represents the distribution of temperature in the ideal well, calculated with  $\varepsilon$  from Eq. 5. With the help of  $\varepsilon$  we get the distribution of temperature in the whole length of the ideal well, using Eq. 1 ( $\tau = T - 11,6$  deg. C)

$$T = 11,6 + \frac{\sigma}{\varepsilon} [1 - \exp(-\varepsilon \cdot z)] \quad (7)$$

where  $z = 50\,000 - H$ .

From the above-mentioned equation we get  $30,1$  °C, this being the value for the temperature of the liquid flowing out, where  $H = 500$  m. Considering that SÜMEGHY measured the temperatures of the water flowing out, the average values calculated by STEGENA on that basis, give outflow temperatures. From this it becomes obvious that in depth of 500 m the not-corrected average temperature has to be same as the temperature of liquid flowing out, calculated from Eq. 7. According to the "a" curve of Fig. 2, the temperature, without correction, in depth of 500 m is  $30,6$  °C, while the Eq. 7 gives  $30,1$  °C. The difference is only  $0,5$  °C, which shows that the reasoning is correct and being sufficiently accurate for the calculation of the terrestrial heat flow.

The true average temperature gradient of the territory investigated being  $\sigma = 4,76 \cdot 10^{-4}$  °C/cm, we get  $35,4$  °C as the average temperature of the virgin rock in the depth of 500 m, and the temperature of the surface is  $11,6$  °C. The true average virgin rock temperature is of course increasing linearly to the depth (Fig. 2 "b").

My measurements of thermal conductivity performed in the Pliocene and Miocene sediments at Nagylengyel [7] where the conditions are similar to those of the Hungarian Plain, showed conductivity values between 0,00307 and 0,00643 cgs, and the average thermal conductivity was of 0,00439 cgs. The porosity of these sandstones, marls and sands was between 5 and 21 per cent 13,8 per cent on the average. The sediments building up the Hungarian Plain are very similar to those of Nagylengyel as far as geological and petrographic compositions are concerned. It may be concluded that the Tertiary formations building up the Hungarian Plain down to a depth of 500 m, the thermal conductivity of these porous and always moist formations varies between 0,003 and 0,006 cgs and its average value can be assumed at least with 0,004 as was the case in Nagylengyel. STEGENA counts with a value of 0,002—0,004, but the lower value stands for dry, porous sediments. Neither in the Hungarian Plain, nor elsewhere, are the porous sediments dry, they are wet and their porous volume is filled up by liquid. Therefore, the thermal conductivity of the wet rocks, in respect to the dry rocks, according to the volume of the pores, may be several times greater than has been proved by my investigations made on samples taken at Nagylengyel (e. g. the thermal conductivity of lower



Pannonian sandstone, the porosity of which is 21,56 per cent, is 0,00281 cgs in dry condition and 0,00643 cgs when saturated with water).

Taking into consideration all the above-exposed, the probable value of the terrestrial heat flow is, taking a gradient of  $4,76 \cdot 10^{-4} \text{ }^{\circ}\text{C}/\text{cm}$  and a thermal conductivity of 0,004 cal/cm, sec. deg. C into consideration,

$$1,904 \cdot 10^{-6} \text{ cal}/\text{cm}^2, \text{ sec.}$$

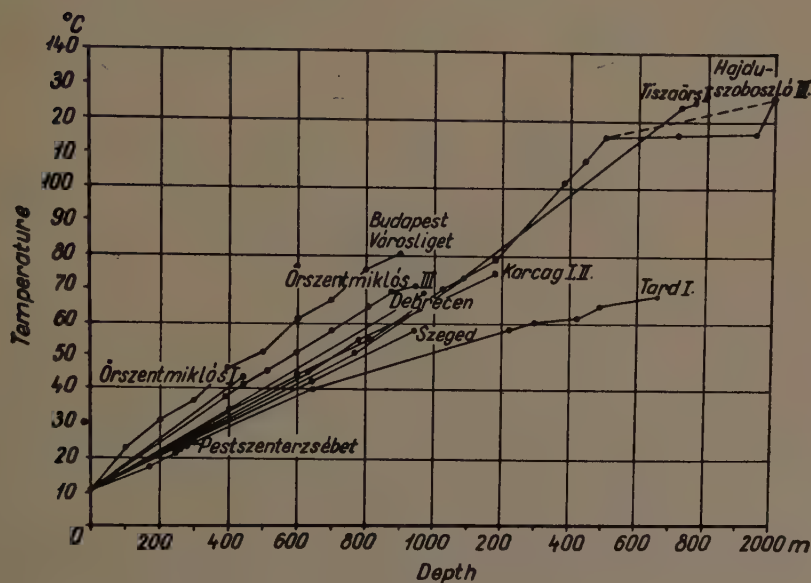


Fig. 4

This value is based on measurements made on 431 wells, plotted on Fig. 1 and therefore characterizes the average conditions of that part of the Hungarian Plain, which is situated inside the present boundaries of Hungary. Due to the great number of measurements it may be considered a quite good average value.

Since the measurements executed by SÜMEGHY, between 1930 and 1945, many deep bore-holes were sunk in the Hungarian Plain down to 2000 m depth [10], for the exploration of oil. The data of temperature measured in these bore-holes give a very good approximation of the original temperature of the formation (marked in Fig. 1 by small triangles). Unfortunately, measurements relative to thermal conductivity are not available. Fig. 4 shows the temperatures as functions of depth, which lead to the following conclusions:

1-st: Neither taking the Zsigmondy-bore-hole in the town park of Budapest, neither the bore-hole of Tard-1 into account which are situated on the border of the Hungarian Plain and show a relatively high, respectively low gradi-

ent of temperature, it can be ascertained by data from the other six bore-holes, that at the depth of 500 m, the virgin rock temperature is between 35 and 45°, that is to say, the corrected temperature of 35,4 °C for a depth of 500 m appears to be rather towards the lower limiting value, than the average. The gradients of temperature, calculated from these, are between  $7 \cdot 10^{-4}$  and  $5 \cdot 10^{-4}$  °C/cm. Calculating with a conductivity of 0,004 cgs, the value of the terrestrial heat flow would vary between  $2 \cdot 10^{-6}$  and  $2,8 \cdot 10^{-6}$  cgs; an average value of  $2,4 \cdot 10^{-6}$  cgs may be taken into consideration. By all accounts it shows, that the original temperature of the formations corrected by my method

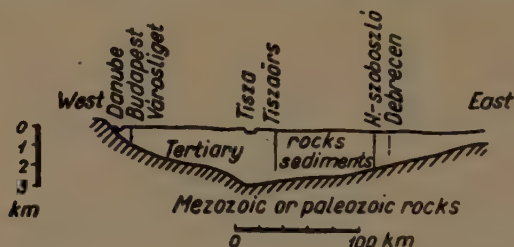


Fig. 5

on the basis of the measurements made by SÜMECHY, and the assumption of an average thermal conductivity of 0,004 cgs cannot result in an exaggeratedly high heat flow. It is even probable that the  $1,9 \cdot 10^{-6}$  cgs value for the heat flow has to be considered as rather the lower limiting value.

2-nd: Beyond 500 m, down to a depth of 1000—1200 m the temperature continues to increase in a fairly steadily and the gradient of temperature remains almost constant and the same as between 0—500 m. It may be assumed that conductivity does not substantially change.

3-rd: The data of only two bore-holes at a depth of more than 1180 m are available; according to these, the temperature gradient suddenly increases towards the depth of 1500 and 1700 m, respectively. The values for the Hajdúszoboszló bore-hole are  $11,2 \cdot 10^{-4}$  °C/cm, those for Tiszaörs  $7,7 \cdot 10^{-4}$  °C/cm. The reason for this is certainly the lower thermal conductivity of the strata (0,0018 and 0,0024 cgs, respectively). The bore-hole of Hajdúszoboszló crosses between 1500 and 2000 m strata of good thermal conductivity and the temperature gradient diminishes to  $2,2 \cdot 10^{-4}$  °C/cm. The thermal conductivity of these strata is of about 0,009 cgs. But it is quite possible that the strata of such high thermal conductivity do not in reality exist and presumably the measurements of temperature between 1200 and 1950 m were inaccurate, or were disturbed by some unknown effects.

Taking the more recent and more accurate measurements into consideration, which — though in a few places only — gave accurate original temperatures of the formations and extend down to a depth of 2000 m, it may be

pointed out that on the territory of the Hungarian Plain the terrestrial heat flow is at least  $1,9-2,0 \cdot 10^{-6}$  cal/cm<sup>2</sup>, sec, or even above this value and its average value is probably  $2,4 \cdot 10^{-6}$  cgs. Its consequence is that the gradient of temperature in the strata of an assumed average conductivity 0,004 cgs (0,0018—0,006 cgs/ on the average varies between  $4,5 \cdot 10^{-6}$  and  $11,2 \cdot 10^{-6}$  °C/cm. Its average value is about  $5,8 \cdot 10^{-4}$  °C/cm. As the Tertiary sediments of a thickness of 1000—3000 m on the whole, deposited on the primary mountain range [11] have normal thermal conductivities, the immediate cause of the relatively high temperature gradient has to be sought in the great terrestrial heat flow.

The reason, why the value of the terrestrial heat flow, observed in the Great Hungarian Plain is almost twice as high as its average value as far which was observed on the surface of the earth [12], has up till now not been explained.

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#### GEOTHERMISCHE UNTERSUCHUNGEN IN DER GROSSEN UNGARISCHENTIEFEBENE

T. BOLDIZSÁR

#### Zusammenfassung

Auf Grund der statistischen Interpretation des Ausflusswassers von 431 Brunnen und unter Berücksichtigung der Temperaturkorrektion konnten die durchschnittlichen geothermischen Verhältnisse der Grossen Ungarischen Tiefebene geklärt werden. Der Wert des durchschnittlichen Gradienten beläuft sich in diesem Gebiete auf  $4,76 \cdot 10^{-4}$  °C/cm. In zehn Bohr-  
löchern bis zu einer Tiefe von 2000 m durchgeführte Untersuchungen ergaben aber einen höheren Wert: 5 bis  $7 \cdot 10^{-4}$  °C/cm. Wird der Wert der durchschnittlichen Wärmeleitfähigkeit der tertiären Schichten mit 0,004 cgs angenommen, ist der terrestrische Wärmestrom wenigstens  $1,9 \cdot 10^{-6}$  cal/cm<sup>2</sup>·sec, wahrscheinlich aber noch höher und kann im Mittelwerte mit  $2,4 \cdot 10^{-6}$  cal/cm<sup>2</sup>·sec angenommen werden.



ГЕОТЕРМИЧЕСКИЕ ИССЛЕДОВАНИЯ НА БОЛЬШОЙ ВЕНГЕРСКОЙ  
НИЗМЕННОСТИ

Т. БОЛЬДИЖАР

*Резюме*

На основании статистической интерпретации температуры воды, изливающейся из 431 колодцев и с учетом температурной коррекции делается попытка объяснить средние геотермические условия Большой Венгерской Низменности. Величина среднего градиента на указанной территории составляет  $4,76 \cdot 10^{-4} \text{ }^{\circ}\text{C}/\text{см}$ . Однако исследованиями, проведенными в 10 скважинах до глубины 2000 м, были предоставлены большие этого градиенты, а именно от 5 до  $7 \cdot 10^{-4} \text{ }^{\circ}\text{C}/\text{см}$ . Принимая величину средней теплопроводимости третичных слоев равной 0,004 cgs, тепловой поток земли будет не меньше  $1,9 \cdot 10^{-6} \text{ кал}/\text{см}^2 \cdot \text{сек}$ , но вероятно больше этой величины и составляет в среднем  $2,4 \cdot 10^{-6} \text{ кал}/\text{см}^2 \cdot \text{сек}$ .

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